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GERMAN AND OTHER SOURCES OF POTASH SUPPLY.*

By **CHARLES H. MACDOWELL, CHICAGO, ILL.**

Up to 1909 the American public had little knowledge of, or interest in, potash. Some remembered that it had to do with soft soap and sore throat, but further they knew not. In 1909-10, the German-American potash war, and the publicity attending hostilities, brought home to America the knowledge that potash was an important article of commerce; that Germany monopolized its production and distribution, and exercised all the prerogatives attending complete control. The present war, with its transportation embargo, has again directed attention to Germany's strength as a potash producer and her present unfortunate situation as a distributor. As a consequence, the search for potash takes on new life and it again becomes a subject of general interest.

My first knowledge of potash came from a study of the German potash exhibit at the World's Fair in 1893. This investigation led to the recommendation that Armour & Co. engage in the manufacture of commercial fertilizers and the fertilizer branch was organized early in 1894. From then to now "potash" has been a live subject.

Two and eight-tenths per cent of the earth's crust consists of potassium oxide. It is an important constituent of feldspar, granite, and other igneous rocks. Potash is valuable commercially in a water-soluble form. In igneous rocks it is locked in so tight that it is of little value and no utilization in a commercial way has been made of these insoluble forms. Potash in water-soluble form is found in large deposits in Germany; in smaller deposits in Austria and Spain; and in brines in some of our western arid basins. The deposits in Germany, Austria, and Spain are concentrations from sea waters containing potash derived from the decomposition of potash-bearing rocks.

It has been found that the amount of potash remaining in decomposed rocks is not the same as that in the original rock. For instance, granite containing originally 5.58 per cent potash only contained 1.49 per cent in the decomposed rock. Syenite containing 6 per cent in the original rock only contained 0.23 per cent in the decomposed rock. Soil also loses potash.

The probable explanation for this loss of potash is the passing of the rain and soil solutions over constantly renewed exposures of the rock, washing out the soluble portion of the potash, which eventually finds its way into the rivers and finally to the sea. It is estimated that one cubic mile of the river waters of the United States contains 20,358 tons of potassium sulphate. It can thus easily be seen that an enormous amount of the available soil potash is being transported by the rivers and deposited in the sea. The sea brines containing salt, potash, magnesium and other salts on concentration drop out the less soluble salt, the mother liquor containing the potash accumulating and later desiccating or crystallizing as veins through rock-salt deposits, over which are formed water-proof covers protecting the deposit and holding it for future use. This briefly is the legend.

GERMAN DEPOSITS AND MINING METHODS.

Potash salts are found in Germany in the Stassfurt, the Hanover, the South Harz Mountain and the West Alsatian sections. Mines are also operating close to Hamburg and Bremen, and lean deposits, with poor cover, are said to extend into Holland. The deposits near Muelhausen are within 25 miles of the French frontier. In the Stassfurt and Hannover sections, the deposits are often found in salt saddles of great depth. The cover has been disturbed and water dangers are present. Several shafts have been lost by flooding. In the South Harz and Alsation sections the layers are more nearly horizontal; the cover has been little disturbed and water troubles are less likely. The depth of the potash and salt deposits from the upper to lower stratum is some 5,000 ft.

Prospecting is done by core drilling. A saturated salt solution is used for drilling, which permits the extraction of a full-sized core of the soluble salt. This method was first used in locating the potash beds of the Aschersleben mine, one of the oldest and largest producing mines. Potash beds have been uncovered in prospecting for oil, coal, and gas. Boring companies are formed; acquire mining rights; prospect; and dispose of proved properties to companies who sink shafts and install concentrating plants.

In Prussia the land owner originally had all the mining rights, while in Hanover the mining rights belonged to the first discoverer of the salt. These laws, of course, have been greatly modified in developing the mines in recent years. A royalty of 60 pfennig per 1,000 kg., or say 15 cts a metric ton crude, is generally paid the owner of the rights. Operating companies are organized either as Gewerkschafts, with 1,000 *Kuxen* or shares of no par value, assessments being made from time to time to complete the work under way; or as Actien Gesellschafts, with a fixed capital in shares of a par value of 1,000 marks.

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*Paper presented Dec. 12 at a meeting of the Chicago Local Section of the American Institute of Mining Engineers.

In shaft sinking the Kind-Chaudron system is generally used. Freezing is resorted to if quicksand is encountered. Shafts are sunk by contract. The average cost of shaft sinking is about $150 per foot. Shafts vary from 300 to 900 m. in depth.

The first potash discoveries were made in Stassfurt. The Stassfurt salt mines are first mentioned in literature in 1227. In earlier years they were used as sources of common salt. Early in the 19th century they were sold to the Prussian government, which started the first bore hole in 1839, striking salt in 1843. The first water that was pumped up from this bore evaporated to about 99 per cent salt, but it soon became very impure with magnesium and potash salts. The first shaft was commenced in 1852 and struck the salt layer in 1857. It was not until 1860 that Professor Francke first advanced the idea of the various strata in salt mines being of importance for other products than salt, and it was in this year that potash was first prepared.

My first visit to a potash mine was in 1906—the mine Sollstedt, near Nordhausen, shipping crude salts and manufacturing muriate. No sulphate was made there because the salts contain no kieserite. Some notes taken at that time may be of interest:

Shaft sinking began October, 1902; finished June, 1904; depth, 705 m.; diameter, 8 m.; iron tubing in sections to salt layers, wood below (many mines use brick through salt layers) Mine dry. Hoisting engine Magdeburg make, 1,000 h.p.; cages double decked; shaft head, iron with concrete thrust blocks. Takes five minutes to descend. Considerable jump to cage at lower levels due to cable stretch. Ventilating fan run by horizontal compound engine of 10,000 cu. ft. per minute capacity. Engine made at Aschersleben, novel valve motion. One direct-connected D. C. motor for lighting and electrical power purposes Power requirements, 1,600 h.p. all told. Burn lignite; mined in neighborhood; little smoke. Separate ventilating tunnel and shaft connecting with main shaft about 75 ft. from bottom. Cover rock largely reddish sandstone. There is a layer of salt clay, anhydrite, and rock salt above the potash deposits, protecting the latter from water danger. Color of potash salt (hardsalt), reddish interspersed with blackish anhydrite and yellow rock salt, these latter layers an inch or so wide. Average potash contents of veins 16.5 per cent K_2O; thickness, 10 m. Salt hard and dry. No timbering necessary Mining under government control. Large chambers laid off with 5-m. supporting pillars. Chambers are cut out to height of 8 ft., width of 20 ft.; potash blasted down and transported in 1-ton cars to shaft. Pillars are permanent, chambers filled in later with mill refuse. Electric and hand drills used. Cars are hauled up grades by electric traction. Mining rights purchased from owners of land on royalty and percentage-of-profit basis. Mine controls right 2.5 miles in three directions. Property abuts Bleichroder mine owned by Prussian government. Deposits figured sufficient to last 800 years.

Shaft ½ mile from mill, located on railroad; transportation, drag chain on industrial track, chain dropping over bail of car; no clutch necessary; speed 2½ miles an hour. Salt, when elevated, conveyed to mill building; dumped to screen over crusher, car being turned upside down. Movable screen bars about an inch apart. These bars work from an eccentric shaft; screen out fine particles and move coarse pieces to crusher. The crushed salt goes to the cookers for concentration, or to the mill for shipment as crude in bulk. Cookers are steel tanks on order of pressure tanks with agitators. The potash is dissolved in a hot solution of magnesium chloride, known as the mother liquor, leaving the salt undissolved. The dissolved hot solution is concentrated and run to large crystallizing tanks, where, on cooling, the potash crystallizes out, the mother liquor being pumped out, heated by exhaust steam and used over again. The waste salt is used for mine filling. Iron crystallizing vats are arranged in clusters of four, surrounded by cement-covered aisles in which are laid industrial-railway tracks. These crystallizing vats cover a considerable acreage. The crystals are shoveled from vats into cars, then to a washing and draining platform, then to storage. Concentrated salts are shipped in bags; mine-run salts in bulk.

This description answers well for other mines, except that in carnallite mines the mother liquors are not used over again and must be discharged into sewers to go to rivers. On this account, carnallite mines can only manufacture a certain predetermined tonnage of concentrated salts; their final liquors are metered, and operations must be curtailed when the river water attains a certain hardness. Carnallite mines make the bulk of the sulphate of potash manufactured, owing to the presence of kieserite necessary for the production of sulphate. Some mines have chemical manufacturing subsidiaries, where electrolytic and chemical processes are used to manufacture other forms of potash and potash combinations.

The method of mining varies according to the way the strata lie in different mines: Where the layers are anywhere near horizontal, continuous ordinary stoping is resorted to, and they usually drift on the bottom of the seam, blasting down from the top and proceeding in all directions from the shaft. Some mines, however, are operated by drifting at the top surface of the stratum and digging out underneath the level. Where the various layers approach the perpendicular, they sink shafts in the material, using inclined skipways to the main shaft. When the deposits are in lenses, "gobbing" is resorted to, filling in with common salt. Power houses and other plant buildings are solidly and expensively constructed. The workman's comfort and safety are thoroughly looked after. Government supervision is everywhere apparent.

COST OF MINE AND COCENTRATING.

Plant.—A mine encountering no unusual difficulties in shaft sinking, and with a shaft depth of say 750 m., with plant site, rail connection, power plant, chemical plant for concentrating, workmen's houses, and all necessary equipment, would cost from $1,250,000 to $1,500,000. A second shaft would cost about $350,000 additional. A fully equipped two-shaft mine, of an annual capacity of say 12,000 to 15,000 tons pure potash, would cost $1,750,000 to $2,000,000.

Cost of Production.—This naturally varies with the quantity and kind of salt mined. Owing to the large number of producing mines, I would say that 36 hr. a week would be average working hours, so the output per mine is small. The cost of mining carnallite averaging 9 per cent K_2O and delivering it to the mill is approximately 4 marks, or say $1, a metric ton of 2,204 lbs.; hardsalts (16 per cent K_2O) would cost 5 marks, or $1.25 per ton. I estimate that a good mine, producing 7,500 tons of pure potash per year, can produce muriate of potash (50 per cent K_2O) at $19 per metric ton; kainite (12.4 per cent K_2O) at $2.40 per metric ton. On a production of 20,000 tons pure potash a year, the same mine could produce muriate at $14 and kainite at $1.60 per metric ton. The overhead charges are included in both estimates. All costs are f. o. b. cars. These costs are probably lower than the average mine cost under present conditions. Some hardsalts mines, on 24 hr. a day mining, claim to have made muriate as low as $10 per metric ton. Restricted mining and short working hours now prevent any such costs being attained. Freights to coast during river navigation average about $1.50 per metric ton, and to American ports $2.50 to $3.00; or say $4 to $4.50 per metric ton from mine to American Atlantic ports.

COMMERCIAL CONDITIONS.

Aside from remote water danger, potash mining is unusually safe mining.

Some years ago, because of overproduction, and with the hope of discouraging new mines on account of expense, a two-shaft law, intended for coal mining and in the interest of safety to miners, was made to apply to potash mines, a reasonable time being given old mines to sink second shafts. The result was unsatisfactory, as old companies would split their holdings, form new companies, sink shafts, and demand new quotas.

For many years, overproduction was the rule and profits the exception. Prussia and other states owned mines. Finally a selling syndicate was formed, all of the then producing mines, including those government owned, becoming parties. Participations in the total sales were agreed on, percentages being figured in thousandths per cent. The syndicate had a life of five years and was headed by a government official. Monetary penalties for violations were exacted. A new syndicate had to be arranged for six months before the expiration of the old syndicate. New mines opening during the syndicate term were taken in and new percentages fixed. Occasionally new mines outside the syndicate would sell below syndicate prices, generally to Americans, but would later enter the syndicate.

On June 30, 1904, one mine refused to enter the new syndicate and for several hours sold freely of bulk salts for five years, finally entering the syndicate subject to keeping such sales as had been made. These sales disturbed the syndicate and steps were taken to make such selling and buying unpopular and unprofitable. Prices on bulk salts were lowered. These reductions automatically lowered the price of the outside mine contracts, as prices were guaranteed. Five-year exclusive contracts were put in effect. Those having bought outside bulk salts were not to be given lowest discounts on bagged goods. They were to be punished financially for having made outside purchases. Secret discounts were given certain favored buyers. Some of the offending Americans "stood pat," and refused to be punished. In due time a new mine opened up and sold these Americans at lower-than-syndicate prices and for a long terms of years, thus defeating the syndicate plans.

In May and June of 1909 I visited Germany and made a thorough inspection of several mines, with the idea of purchase. At that time the various syndicate members were negotiating for the renewal of their syndicate, which expired June 30 of that year. Rumors of serious dissentions were prevalent and the prophecy was made that the syndicate would not be renewed. There were too many mines and too little business. The prophecy proved true, as, at midnight of June 30, members could not agree and free trading was in order. There were several American buyers in Berlin, and, for two hours, a considerable business was effected by seven mines at a material reduction from old syndicate prices and for a term of years. The Prussian government then exerted sufficient influence to stop further trading, for the time. It immediately became known that a large business had been done and mines not participating began to exert pressure to force sellers to cancel their contracts. Thus began the potash war of 1909-10. A cabinet member discussed the situation in the Reichstag. The press took up the refrain and the stage was set for an interesting commercial comedy. The first suggestion was to levy an export tax on these particular American contracts, but that was decided to be too openly discriminating. One of the contracts contained a clause reading, "Any import or export tax or other governmental charge should be paid by the buyer," meaning any uniform tax, applicable to all business. Here was a legal peg: "Other governmental charge." A law was introduced, and finally passed, declaring potash to be a monopoly; that every producer was entitled to a certain percentage of the total business (the percentage to be fixed by governmental agencies), and that any producer selling more than his fixed percentage should pay a supercontingent tax amounting to more than the purchase price of the contracts. This, of course, only applied to mines selling to America, who had sold large tonnages, and could only apply to American purchasers. Our State Department protested vigorously, and a tariff war was threatened. The situation was strained. For some months these taxes were paid by the buyer under protest. Finally the Americans accepted the situation and a peace was concluded. The amount involved ran into many millions. As a part consideration for canceling the contracts, a percentage of the tax paid under protest was refunded American buyers by the German government. Friendly relations now exist.

During the hostilities, I made the suggestion to the Washington authorities that our government should make a search for potash. Appropriations were made, and the investigation is still under way.

On July 1, 1909, there were 52 producing mines in Germany. Our latest reports are that 160 mines are now producing and from 30 to 40 are under construction. This condition has naturally followed the monopoly legislation and fully $150,000,000 has unnecessarily been invested in the German potash industry. Thirty of the best mines could take care of the world's needs.

UNITED STATES' CONSUMPTION OF POTASH.

Statistics of the year 1912 show 11,164,000 tons of crude potash mined in Germany. This is equivalent to about 1,100,000 tons of pure potash. Of this, the United States takes from 245,000 to 250,000 tons. The fertilizer industry uses from 235,000 to 240,000 tons and the chemical industry, 12,000 to 15,000 tons. The average monthly arrivals have been about 20,000 tons. From Aug. 1 to Dec. 1, 1914, some 10,000 tons of pure potash have come in, as compared to a normal receipt of 80,000 tons. Burlap bags are now becoming scarce, and concentrated salts will have to be shipped in casks, or taken in bulk, if shipped. The outlook is not favorable for heavy winter shipments. The fertilizer manufacturer probably has enough on hand to carry him through his spring season on a restricted-percentage basis. The chemical manufacturer is in about the same situation. Should the war continue through the summer, the present rate of shipment, if continued, would take care of only a small part of our necessities.

OTHER SOURCES.

Austria.—Small, partly developed deposits exist in Galicia, Austria, near Kalusz. Not to exceed 1,000 tons a year of pure potash has been produced—Austria importing the bulk of her requirements from Germany. It is probable that German influence has prevented the development of these deposits. It would not be good sense for any great investment to be made in Austria to produce potash when one considers the close relations existing between Austria and Germany and the large investment Germany has made in the potash industry.

Spain.—Some three years ago, we received from Europe a mining engineer's report on a potash discovery made in connection with some salt developments in Spain, near Sauria. Later the discovery became public. Analysis of the salts found showed a good proportion of potash, fairly amenable to refining. Mining reports and maps submitted to us led me to believe that, owing to shallow depths and poor cover, shaft mining in the deposit reported on would be dangerous. Brining might, however, be resorted to. Since that time, further discoveries have been made; concessions have been granted to companies to prospect; and Spain may become a potash-producing nation. That country should be a good distributing center, and, if the government does not, by export taxes or other restrictive measures, kill the goose that lays the golden egg, Spanish potash may come on the market. This cannot be for several years, however, and does not help in the present predicament. The potash seems to be there.

Peru.—I have examined reports showing fair-sized and workable deposits of nitrate of potash in Peru. One of these deposits has been worked in a small way. It is close to transportation and should be further investigated.

AMERICAN POSSIBILITIES.

Some potash can be made as a by-product from other manufacturing industries. Practically no progress has been made in this direction in this country.

The sugar-beet tonnage in the United States totals 5,147,000 tons. Sugar-beet wastes from this tonnage could produce 30,900 tons of potassium carbonate, equal to 15,440 tons of pure potash.

Raw wool contains up to 20 per cent potash salts. The wool clip of the United States weighs 298,000,000 lb. In wool scouring 7,450 tons of potassium carbonate or 4,470 tons of pure potash is washed out and lost. This could be largely recovered. Much raw wool from Australia and other countries is imported, and the potash from the handling of this wool could also be saved.

Potash from Cement Burning.—Many cements before clinkering contain small percentages of potash, say 0.1 to 0.25 per cent. In burning this is volatilized. While the percentage is small, the tonnage is so large it figures quite a production on paper.

Many experiments have been made to recover this volatilized potash. It has been worked out to a point where the physical part of the operation is a success. It consists of condensing the volatilized potash in chambers and dust collectors similar to the bag house used in smelters. Up to the present time, however, no cement manufacturer has produced potash as a by-product. Possibly the investment expense attached to its recovery figures against it. I have no data on this.

The industry is a possible source of a considerable tonnage of potash and in case of necessity can be utilized without any extensive changes in present methods of manufacture. Possibly cheaper recovery methods may be found.

At one time considerable carbonate of potash was derived from the ash from burning cotton hulls. These are now used for fodder, so no potash could be obtained from that source.

A few years ago tobacco stems were distilled destructively for nicotine and other products. The ash from this material contained high percentages of carbonate of potash. This method of handling has now been discontinued, but the potash in the ground tobacco stems is saved and used for fertilizing purposes.

This about exhausts the by-product possibilities as far as I know.

Hardwood ashes and other ashes are gathered and used in fertilizing for their potash contents. City garbage contains appreciable percentages of potash. This garbage in many cities is recovered and used for fertilizing purposes.

GOVERNMENT WORK.

Following the 1910 appropriations, the Geological Survey and the Department of Agriculture immediately began their work. One of the first suggestions made was that the giant kelps of the Pacific Ocean might be a source of supply. As far back as 1904 the manager of our Pacific Coast fertilizer business called our attention to these kelps and their large potash contents when figured on a dry basis. He proposed to burn them, recover the nitrogen and iodine, and use the ash. He went as far as to gather a few tons of kelp and burn it. Later we did some research work in Chicago, not only on the Pacific but also on Atlantic Coast kelps, with a view to complete utilization, with rather satisfactory results. We decided, however, at the time that the cost of gathering the wet kelp and handling it made it a rather difficult thing to figure out profitably; that we were dry-land people and a fleet of boats would be needed to gather any tonnage; and that there was a little chance of protecting any process we might develop. Further, it was so easy to get the German product, that the matter was dropped. The total tonnage is no doubt large, but the kelp has a small per-ton value when wet and its gathering and preparing present a problem difficult to solve with financial success. A McCormick may come along with a kelp reaper, presser, and binder that may give the solution. The government has done splendid work in charting the beds and in obtaining other data. These beds are more or less continuous from Vancouver to San Diego, with several important concentrated areas, one of which is off the port of Los Angeles and another off the coast of Seattle.

Authorities differ as to the relative importance of these two beds, but apparently those along the northern coast are more important than those to the south.

Little real work has been done in the harvesting and utilization of this kelp. Several stock-selling companies have been formed, and a company operating at Long Beach, Cal., is producing about 500 lb. of combined salts per day. The general plan has been to cut the kelp and allow it to wash to shore, and although some success was obtained with a harvesting boat, no attempt has been made toward extensive operations.

The question has been gone into quite thoroughly from time to time, and unless definite outlets can be found for by-products such as iodine, tar, and so-called gums, it is doubtful if the utilization of kelp can be made commercial.

A second source of potash on which the government has reported is Searles Lake, Cal. At this point there is a large dry lake of several square miles in extent upon which a company is now erecting an experimental plant for the production of the various salts found in the brine underlying the surface.

This brine is pumped from wells sunk through the solid crystals and contains about 35 per cent solids, 5.35 per cent in the form of potassium chloride. The plant which is now under construction is expected to be in operation by Jan. 1, 1915, and this plant will produce daily: 5 tons of potassium chloride; 5 tons of carbonate of soda; 2½ tons of borax; 15 tons of common salt; 10 tons of sulphate of soda.

The company has in mind an ultimate plant that will be 100 times this capacity, to be constructed in units similar to the plant now under construction, so that it will be some time before any considerable quantity of potash will be produced. The supply of brine is apparently large, and under the proposed plan should last for a good many years. The entire success of the undertaking would seem to lie in the outlet for the various salts produced, besides potash. I have followed the development of this project from its inception and it looks to me as if it should work out and become an important source of supply. The development is in strong hands financially.

Alunite.—A deposit of alunite located near Marysvale, Utah, is described in *U. S. Geological Survey Bulletin, No.* 511. Alunite is a double sulphate of potash and alumina with the following theoretical composition: Al_2O_3, 37 per cent; SO_3, 38.6; K_2O, 11.4; and H_2O, 13 per cent. The Custer-Marysvale deposits are quite pure for large deposits and rather closely approximate the theoretical. A calcining process followed by leaching releases about 85 per cent of the potash as sulphate, as reported by the government. Large quantities of hot water are required for leaching. Owing to transportation difficulties and to the necessity of finding a market for a big tonnage of impure alumina, the property has not yet been developed. Large capital expenditure would be required, which would hardly be justified from the potash standpoint alone.

Potash from Feldspar.—The first recorded work on the recovery of potash from feldspar was done by Tilghman about 1845; the first United States patent was obtained by Bickel in 1856. Various investigators have been working in this field practically ever since, receiving stimulus from time to time as the potash question became acute.

In recent years, research on this subject has been along four general lines: First, by the use of natural agencies, such as heat, bacteria, carbon dioxide, etc.; second, wet chemical methods, such as solution in alkalies or acids; third, dry reactions in which the potash is volatilized; fourth, dry heat reactions in which the potash is converted into a water-soluble form. All of these methods have been more or less successfully operated in the laboratory, but up to date their cost has been prohibitive to commercial development.

The fact remains that there is practically an unlimited source of potash in this country in the igneous rocks, particularly those of the feldspathic type, and no doubt eventually some of these processes will be made commercial, probably through a proper usage of the by-products produced in the recovery of the potash.

The use of feldspar in connection with the manufacture of white cements seems to me to be the most encouraging. An Austrian process looks rather good as far as it has gone. The cost of mining feldspar is considerable. A cheaply mined deposit and the necessity of having this deposit in a locality suitable for the manufacture and distribution of cement would be the controlling features in such an industry.

Leucite.—The leucite hills of Wyoming contain large quantities of potash in an insoluble form. As far as I know, no serious work has been done on this material. It is claimed that by a simple process the potash can be made available for plant food, but in the form offered it is not soluble in water and could not be used in the fertilizer industry, as the various State laws require water-soluble potash. Dana gives an analysis of leucite from the Albani Mountains, containing 21.48 per cent of K_2O. The leucite hill deposits, according to an analysis from the Armour laboratory, contain 11.34 per cent K_2O. Other analyses of different samples show even higher potash contents. The quantity is practically inexhaustible.

Other Brines.—The brines of several alkali lakes and ponds in western Nebraska contain appreciable percentages of K_2O. A government analysis of one of these showed 3 per cent K_2O in the water. An analysis of a sample of the solids from one of these lakes made by the Armour laboratory showed 15 per cent K_2CO_3 and 33 per cent K_2SO_4. The Geological Survey reports in substance:

> A number of alkali ponds and lakes existing in Cherry, Sheridan, Morrill, Garden and Boxbutte Counties, Nebraska, have been examined and in some of these the percentage of potash is as high as 30 per cent of the soluble material. Although the total potash in solution is large it is disseminated in the muds so that profitable extraction will prove difficult. Some of these deposits are near transportation.

Within the last two years, well drillers in Texas have reported the presence of appreciable quantities of potassium in brines at depths around 800 ft. Dr. Carl Scholz, of the Rock Island Railroad, reports that from these drillings he is led to the belief that east of the western boundary line of Oklahoma, in the vicinity of Magum, a potash deposit may lie within easy reach.

Development work, principally deep-well drilling, is also being done in various sections of the country, especially in the West and Southwest. In most cases the object is to find dried-up lake beds containing soluble potash salts or brines from these sources as well as those draining potash-bearing rock territory. The commercial utilization of such workings will depend, of course, upon the extent of the potash-bearing areas and their concentration.

SUMMARY.

In by-product lines, the sugar manufacturer and the wool scourer might spend some money on solving their problem. The cement manufacturer could well afford to investigate potash manufacture from potash-bearing rocks in connection with cement manufacture.

If potash is to be produced in this country in quantity, some one must spend some money. There has been a noticeable reluctance on the part of American capitalists to finance serious research work, or prospecting by deep core drilling. To begin with, our mining laws and mineral withdrawal possibilities are discouraging. A German potash mine controls several thousand acres of mineral rights. The necessary capital investment would not be justified if this control was not legally obtainable. Potash mines with the necessary concentrating plants are expensive and a large acreage control is necessary. Deep core drilling or other development work on government lands by private individuals would not be justified during the present stage of development of the art of conservation as practiced by our legislators. A positive control of acreage must go with such preliminary work.

There is a large market for potash and the demand is growing. Possibly the lever of necessity may develop sufficient power to overcome the prevailing inertia. Up to now Searles Lake is the only nearby producer on the map.

HIGH PRICES FOR ACETIC ACID IN ENGLAND.

Much of the vinegar used in the United Kingdom in recent years has been manufactured from acetic acid imported from the Continent. This supply has now been cut off and the price of "60 per cent acid," chemically pure for the manufacture of vinegar, has risen to $140 per ton, which is about $50 above the normal price. Nearly all the Continental exporters of the acid shipped cash against documents, and the English importers are therefore used to these terms.

Owing to the scarcity of labor due to military levies the gathering of most of this year's yield of Asia Minor gum tragacanth was prevented. The local stock remaining from last year does not exceed 30 tons. There has been little demand this year from European buyers, but some small shipments have been made to the United States. Prices are abnormally low, but increased freight rates bring them to almost the usual level. Good natural gum sells for 38 cts. per pound c. i. f. New York. The white variety is slightly dearer.

California's crude-oil production in 1914 was 103,623,695 bbls., against 97,867,148 bbls. in 1913.

NITROGEN OF PROCESSED FERTILIZERS.*

By ELBERT C. LATHROP.†

Organic compounds have lately taken on a deeper significance in their relation to the complex problems of the soil and of crop production, for not only do they affect the physical conditions and chemical reactions of the soil but they also have been shown to be directly connected with fertility or infertility, some of them being essentially beneficial to the growth of plants, while others are distinctly harmful. Of the organic compounds thus far isolated from soils, a large number contain nitrogen, and of these nitrogenous substances, some have been found rather widely distributed in soils varying as to location, climate, methods of cropping, etc. These nitrogenous compounds occur either as plant constituents or arise from the decomposition of plant or animal protein, brought about by the various biological and biochemical agents in the soil. Not only compounds of this class found in soils but also many other protein decomposition products have been studied, both alone and in conjunction with the three fertilizer elements, in respect to their action on plant growth, and they have been shown in a number of cases to exert a beneficial influence; furthermore, these complex compounds are available for use by the plant without first being changed by chemical or biochemical means into ammonia and then to nitrates.

That these facts have an immense practical bearing on fertilizers and the fertilizer industry, both from the standpoint of the producer and of the consumer, is at once obvious. The old high-grade nitrogenous fertilizers, such as cottonseed meal, dried blood, fish scrap, etc., are being used more and more for feed purposes, and the time can not be far distant when their use as fertilizers will cease to be economic; thus a necessity for other and cheaper fertilizers of this type arises. Coupled with this is the desire of the chemist and the manufacturer to utilize in one way or another all waste products, whatsoever their nature, so that the number and kinds of nitrogenous materials which are used in the manufacture of fertilizers is on the increase. Described in the patent literature and found on the market are a large number of fertilizers which may be characterized as "processed," that is, the crude materials, not in themselves permissible as fertilizers, are made to undergo some decided chemical change to render them suitable as plant nutrients. It has been found that the "availability" of the crude substances is nearly always greatly increased by such processing and that a much larger percentage of the nitrogen in the finished product is soluble in water, although the actual chemical changes produced seem to have received little attention. The chemical compounds in processed fertilizers which are here shown to have direct fertilizer significance have not been determined, other than to show that ammonia is formed during processing and that ammonia is more readily produced from the processed goods.

Since the wastes from which this type of fertilizer is made contain more or less protein, or proteinlike substances, it seemed quite obvious that the finished fertilizers must contain more or less of the chemical compounds which would arise by such treatment from pure proteins in the laboratory. Since the action on plants of many of this class of compounds has been determined it is evident that the finding of such compounds in the fertilizers would throw much light on the question of the "availability" of the nitrogen in the fertilizer itself.

BASE GOODS A TYPE OF PROCESSED FERTILIZER.

For a chemical study of processed fertilizers a sample of "wet-mixed" or "base goods" fertilizer was chosen as a representative of this type of fertilizer material. The base goods was obtained directly from the factory for use in this investigation. This fertilizer is made by the treatment of various trade wastes and refuse, such as hair, garbage tankage, leather scraps, etc., with rock phosphate and the requisite amount of sulphuric acid. These materials are mixed together in a "den" and the resulting mass is allowed to stand for several days, until it is cool enough to be conveniently handled. In the course of the reaction the mass reaches a temperature approximating 100° C., and the identity of the original substances is almost or entirely lost Under these conditions it is certain that more or less hydrolysis of the proteins in the crude materials takes place, with the formation of proteoses, peptones, polypeptides, or the simple amino acids, the kinds and number of products formed necessarily depending on the proportion of the different proteins in the original materials, on the amount and strength of the acid, the length of time of the reaction, and the temperature reached during the treatment.

Harwell and Pember have recently made a study of base goods in order to determine the availability of the nitrogen contained in it as compared with that of the high-grade nitrogenous fertilizers. The product which they used was made from hair tankage, garbage tankage, and roasted leather, together with rock

TABLE I.—TOTAL NITROGEN IN CRUDE MATERIALS AND FINISHED PRODUCT (HARTWELL & PEMBER).

	Per cent.
Hair tankage	6.28
Roasted leather	6.49
Garbage tankage	2.87
Base goods, including the above	1.68
Water soluble nitrogen in base goods	1.28
Water insoluble nitrogen in base goods	.40

TABLE II.—PERCENTAGE OF THE TOTAL NITROGEN PRESENT IN DIFFERENT FORMS (HARTWELL & PEMBER).

	When mixed.	When taken from den.
In ammonia	6.5	14.3
In water soluble organic matter	7.8	57.7
In water insoluble organic matter	85.7	28.0

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*From The American Fertilizer.

phosphate and sulphuric acid. From their report the following figures for the analysis of the crude materials used in producing the fertilizer and of the finished products are taken.

The experimental work of the present investigation was along two separate lines: (1) Analytical, involving total nitrogen determinations and the separate estimation of the various forms in which nitrogen may occur; (2) a determination of the definite chemical compounds present in the fertilizer by suitable methods of isolation and identification.

THE CHEMICAL EXAMINATION OF BASE GOODS.

Total Nitrogen and Ammonia.

Total Nitrogen.—The total in the base goods was determined by the Kjeldahl-Gunning-Arnold method and was found to be 1.61 per cent.

Ammonia.—Considerable difficulty was experienced in obtaining concordant results in the determination of the nitrogen in the form of ammonium salts. Boiling weighed amounts of the base goods with water and magnesium hydroxide, according to the official method, for the determination of ammonia in fertilizers, did not give duplicate results sufficiently close for the purpose of this research. Owing to the acidity of the sample, it was impractical to use barium carbonate, but litharge was used with varying results. Finally, the determination was made by using the vacuum distillation method, which gave concordant results. This method, which gives only the nitrogen found as ammonia or as ammonium salts, is used for the determination of amide nitrogen in the products of acid hydrolysis of proteins. A weighed quantity of the fertilizer was placed in a Claisen flask connected up with a cooled receiver of 1 liter capacity and a small guard flask of 200 cubic centimeters capacity. Both flasks contained 0.1 N sulphuric acid. To the fertilizer was added 100 c. c. of neutral 95 per cent alcohol and 100 c. c. of distilled water, together with enough 10 per cent suspension of calcium hydroxide to make the mixture decidedly alkaline in reaction. The ammonia was then distilled under a pressure of from 10 to 12 mm., the temperature of the bath not exceeding 40° C. In the table which follows are given the results obtained by the three methods here used for the determination of ammonia.

TABLE III.—NITROGEN IN THE FORM OF AMMONIA OR AMMONIUM SALTS.

	% of base goods	% of total nitrogen in base goods
Magnesium hydroxide distillation...	0.380	23.60
	.389	24.16
Lead oxide distillation.............	.394	24.47
	.420	26.09
Vacuum distillation	.374	23 23
	374	23.23

An examination of these results shows that by boiling with magnesia or litharge, somewhat more nitrogen is found as ammonia than really exists in this form in the base goods. It is therefore probable, that there are in the base goods nitrogenous compounds which are broken down into ammonia by the action of these alkaline reagents at a temperature of 100° C. The use of magnesia at boiling temperature for the purpose of determining the amount of ammonia split off by acid hydrolysis from certain proteins which contained cystine, was found to give unreliable results. The reason for this was found to be that magnesia under such conditions changes a part of the amino nitrogen of cystine into ammonia. In this laboratory it was also found that by boiling cystine with lead oxide one of the amino nitrogen groups of this compound was split off almost quantitatively, with the concurrent splitting off of hydrogen sulphide. Furthermore, it has been shown that if the amide nitrogen from protein hydrolysis is determined by distillation with a weak alkali, such as calcium hydroxide, at a temperature not to exceed 40° to 42° C. in the bath and at a pressure of from 10 to 12 millimeters, no decomposition of cystine takes place.

In the manufacture of base goods the hair which is used contains proteins which on acid hydrolysis yield a high percentage of cystine. This fact, together with the analytical results just discussed, suggest rather strongly that there is present in the base goods more or less cystine, although this evidence can not be considered conclusive, since it is possible that in such a heterogeneous mixture there may be present other nitrogenous compounds which would be decomposed by magnesia or litharge with the liberation of ammonia.

NITROGEN PARTITION.

For the purpose of determining the different forms of nitrogen present in the base goods the method of Van Slyke was followed in its essential details, except that the determination of cystine, was not made. The method for the determination of this compound, according to the procedure used by Van Slyke, depends not upon a nitrogen determination but upon the determination of the amount of sulphur in the compounds precipitated by the phosphotungstic acid. This determination when made on the hydrolytic products of acid digestion of pure protein may give quite satisfactory results, but the raw materials from which base goods are made contain many organic compounds other than proteins or protein decomposition products, and this is of course particularly true in the case of garbage tankage. It is well known that many plant and animal substances contain sulphur in a variety of linkages, and garbage tankage no doubt contains sulphur in other forms than that of cystine. The hair and leather used have both undergone some decomposition before the acid treatment and it is not impossible that the cystine originally present in the proteins may have changed into sulphur compounds of a different chemical nature. No doubt some sulphur compounds other than cystine are precipitated by phosphotungstic acid, so that a determination of cystine depending on the sulphur content of the phosphotungstic acid precipitate would be of uncertain value in dealing with material of unknown origin and of such a heterogeneous character as fertilizer goods.

It should also be stated that although the results from the Van Slyke analysis are expressed in the usual way, arginine N, histidine N, etc., that it is not intended to convey the impression that these fractions contain pure arginine, histidine, etc., since as will be shown later, other compounds are included under these analytical terms. However, the nitrogen so expressed is that which is contained in compounds which give the various reactions upon which the Van Slyke method depends.

Two 20-gram samples of base goods were extracted for analysis. The first sample was extracted with boiling water until the extract ceased to give an acid reaction. The second sample was boiled for 24 hours with hydrochloric acid, sp. gr. 1.115, the resulting solution was filtered by suction and the insoluble residue washed with hot water until the washings ran free from chlorides. The two extracts were then concentrated to the consistency of a syrup in vacuo to expel the free volatile acid, and each was finally made up to volume of 250 c. c.

Total Nitrogen.—Total nitrogen in solution was determined by subjecting 50 c. c. of the solution to Kjeldahl analysis. The water extract contained 1.372 per cent and the hydrochloric acid extract 1.435 per cent of the base goods.

Amide Nitrogen.—Amide nitrogen was determined by distilling in vacuo the remaining 200 c. c. of solution, to which were added 100 c. c. of 95 per cent alcohol and 20 c. c. of a 10 per cent suspension of calcium hydroxide, as described under the determination of ammonia. The water extract contained 0.374 per cent and the hydrochloric acid extract 0.882 per cent.

Humin Nitrogen.—The residue from the amide nitrogen determination was used for the determination of humin nitrogen. The percipitate, formed by the addition of calcium hydroxide, was filtered off and washed with distilled water in the same manner in which Van Slyke directs that the phosphotungstic acid precipitate be washed. The washing was continued until no reaction for chlorides or alkalinity was obtained. The nitrogen remaining in the precipitate and in the filter paper was then determined by Kjeldahl analysis. The humin nitrogen was 0.031 per cent for the water extract and 0.074 per cent for the hydrochloric acid extract.

Diamino Acid Nitrogen.—The combined filtrate and washings from the humin precipitate were neutralized with hydrochloric acid, concentrated in vacuo to a volume of about 100 c. c. and then transferred to a 300 c. c. Erlenmeyer flask. To this solution were added 18 c. c. of concentrated hydrochloric acid together with 15 grams of purified phosphotungstic acid and the whole diluted with water to a volume of 200 c. c. The flask was placed on a steam bath and heated until the phosphotungstates were almost redissolved, when it was set aside for 48 hours in order to allow them to rescrystallize and fully precipitate. The precipitate was then filtered, washed, and dissolved in 45 per cent sodium hydroxide as described by Van Slyke. The phosphotungstic acid was precipitated with barium chloride and filtered off. The filtrate and washings from this precipitate were concentrated in vacuo and made up to a volume of 200 c. c.

Arginine Nitrogen.—Arginine nitrogen was determined in 100 c. c. of this solution by boiling with 12.5 grams of solid potassium hydroxide for six hours and collecting the ammonia formed in 0.1 N sulphuric acid. Under these conditions one-half of the nitrogen in the arginine and 18 per cent of the nitrogen of cystine is split off as ammonia.

Total Nitrogen in the Diamino Acid Solution.—Total nitrogen in the diamino acid solution was found by subjecting the solution remaining after the arginine determination to Kjeldahl analysis and adding to the ammonia so obtained the amount obtained from the arginine nitrogen determination.

Amino Nitrogen.—Amino nitrogen was determined by means of the Van Slyke apparatus.

From these figures the nitrogen was calculated as arginine N, histidine N, and lysine N, according to the two formulas:

(1) Histidine N = 1.667 non-amino N — 1.125 arginine N.

(2) Lysine N = total N — (arginine N + histidine N).

The results obtained were as follows: For the water extract arginine 0.111 per cent, histidine nitrogen 0.117 per cent, and lysine nitrogen 0.081 per cent; for the hydrochloric-acid extract they were 0.104, 0.070. and 0.117 per cent, respectively.

Total Nitrogen of the Monoamino Acids.—To the combined filtrate and washings from the phosphotungstic acid precipitate 45 per cent caustic soda was added until the solution became turbid by the precipitation of lime; acetic acid was then added until the solution cleared. This solution was placed in a 500 c. c. flask and made up to the mark. Total nitrogen was then estimated in 100 c. c. portions, using the Kjeldahl method.

Amino Nitrogen.—Amino nitrogen in the form of monamino acids was determined by use of the Van Slyke apparatus.

From the two figures obtained the amount of nitrogen present as *non-amino nitrogen* in monoamino acids was found by difference. The amino nitrogen in the form of monoamino acids in the water extract was 0.543 per cent and in the hydrochloric acid extract 0.546 per cent. The non-amino nitrogen in the monoamino acid fraction of the water extract was 0.114 per cent and in the hydrochloric acid extract it was 0.133 per cent.

Van Slyke has shown that certain corrections must be applied in the method, owing to the fact that the phosphotungstates of the diamino acids are slightly soluble, and these corrections have been applied just as though the fractions contained only the hydrolysis products of pure proteins. In Table V the combined results of the analyses are given.

The above analytical procedure which separates the nitrogen into different groups, gives results that can only be rigidly interpreted when the products of the acid hydrolysis are known. The results of the analysis of base goods by this method can only be clearly understood when further facts regarding the compounds, in which the nitrogen is contained, are discovered. A description of the methods used in isolating and identifying certain of these compounds follows.

ISOLATION AND IDENTIFICATION OF DEFINITE COMPOUNDS FROM THE PROCESSED FERTILIZER.

Ten pounds of base goods were extracted by boiling for one hour with 20 gallons of water in a steam-jacketed kettle. The solution was filtered from the insoluble residue, made exactly neutral with caustic soda, the precipitate formed filtered off, and the filtrate concentrated in a steam kettle to a volume of about 3,500 c. c.

This solution contained phosphates, sulphates, and much other mineral matter. In order to separate as much of these salts as possible from the organic compounds a cold saturated solution of barium hydroxide was added to the solution until no further precipitation took place. The heavy precipitate which formed was filtered off by suction and washed many times with water. The filtrate was exactly neutralized with sulphuric acid and concentrated to a volume of about 2,000 c. c. After cooling, this solution was made acid to 5 per cent with sulphuric acid and a solution of phosphotungstic acid was added to slight excess, and the mixture allowed to stand.

After three days the precipitate which formed was filtered off and washed with water containing about 5 per cent sulphuric acid and a little phosphotungstic acid. The precipitate was carefully dissolved in 45 per cent caustic-soda solution, using phenolphthalein as an indicator and adding at no time more than two drops of the alkali solution. Water was added so that a volume of about 1,500 c. c. was reached, and barium hydroxide solution was added until the phosphotungstic acid was precipitated. After filtering off the barium phosphotungstate, the free alkali was just neutralized with sulphuric acid, and the solution was then evaporated almost to dryness with barium carbonate in order to expel all of the ammonia. The residue was taken up in about 1,000 c. c. of hot water and filtered, and the precipitate washed with hot water. The filtrate was placed in a 5-liter flask and treated while hot with solid silver sulphate, which was added slowly until the solution contained sufficient to give a yellow precipitate, when a drop was removed and tested with a solution of barium hydroxide. The solution was then filtered, and the separation of the three hexone bases was carried out according to the method of Kossel and Kutscher. The solution was cooled to 40° C. and saturated with finely powdered barium hydroxide. The precipitate which was formed was collected and stirred up in a mortar with solid barium hydroxide, when it was again filtered off and washed with barium-hydroxide solution. This precipitate contains the silver salts of histidine and arginine, while the filtrate contains the lysine.

Lysine.—The above filtrate was acidified with sulphuric acid and freed from silver with hydrogen sulphide. Lysine was precipitated from this solution as the phosphotungstate, and the free base was obtained by decomposing this salt with barium hydroxide. From a concentrated solution of the base, which was strongly alkaline in reaction and which showed no tendency to crystallize on standing, the picrate salt was prepared. This compound showed the solubility, characteristic crystalline appearance, and properties of lysine pictrate. When taken up in boiling water and allowed to crystallize slowly, it formed in rather large yellow prisms, but when in small amount the crystals assumed a fernlike appearance. The lysine was further identified by the preparation from the picrate of the hydro-chloride salt, $C_6H_{14}O_2N_2.2HCl$, and the platinum chloride salt, $C_6H_{14}O_2N_2.H_2PtCl + C_2H_5OH$.

The silver precipitate which would contain the arginine and histidine was suspended in water acidified with dilute sulphuric acid and broken up with hydrogen sulphide. The silver sulphite was filtered off, the sulphuric acid was removed with barium hydroxide solution, and after filtering the solution was made slightly acid with nitric acid. Silver nitrate solution was added until a test drop with barium hydroxide gave a yellow precipitate. Histidine was completely precipitated as the silver salt by the careful addition of barium hydroxide solution. The precipitate was washed with barium hydroxide solution until the washings ceased to give a test for nitrates.

Histidine.—The histidine silver was suspended in water acidulated with sulphuric acid and treated with hydrogen sulphide. The procedure described by Kossel and Kutscher was followed, and the histidine was finally separated as the dihydrochloride salt. The method of obtaining this compound and the characteristic crystalline form of the dihydrochloride salt are sufficient to establish its identity as histidine.

Arginine.—The method of isolating arginine is simply a further step in the method used in the isolation of histidine. Arginine was isolated first as the acid nitrate salt, which crystallized in the form of plates, and was further identified by preparing the neutral nitrate salt and copper nitrate salt both in characteristic crystalline form.

Monoamino Acids.—The filtrate from the phosphotungstic acid precipitate was made alkaline with barium hydroxide in order to remove the sulphuric and phosphotungstic acids, and filtered. The filtrate was concentrated and nearly neutralized with sulphuric acid. This slightly alkaline solution, about 500 c. c. in volume, was treated by boiling with freshly prepared copper hydroxide, and was then poured into about 3,000 c. c. of 95 per cent alcohol and allowed to stand over night, in order that the insoluble mineral matter might settle out. The deep-blue alcoholic solution was then filtered, the insoluble salts redissolved in water, and reprecipitated by pouring into alcohol as before. The alcoholic solutions were combined and evaporated to dryness, the residue was taken up in hot water and the copper removed by treatment with hydrogen sulphide. After filtering from the copper sulphide, the solution, which contained considerable color, was boiled with animal charcoal. The filtered solution was made faintly alkaline with ammonia and treated with freshly precipitated copper hydroxide, keeping the volume of the solution at about 1,000 c. c. The solution was filtered from the excess of copper hydroxide and evaporated to dryness on the steam bath. The solid residue was then scraped from the sides of the dish and extracted in a Soxhlet extractor with absolute methyl alcohol until no further blue color was imparted to the alcohol.

Leucine.—The alcohol insoluble portion was dissolved in a large volume of boiling water and the copper removed with hydrogen sulphide. The solution was filtered, boiled down to a volume of about 50 c. c. and treated with ammoniacal lead acetate until no further precipitation took place. The precipitate was washed with 95 per cent alcohol and was finally decomposed with hydrogen sulphite after suspending in water. On concentration of a portion of this solution the characteristic crystals of impure leucine formed. These crystals separated in concentric nodules closely resembling fat, but which were composed of concentrically grouped highly refracting needles. These crystals were redissolved in water and added to the original solution which was boiled up with animal charcoal until the color disappeared. The leucine was then purified as before by the formation of the copper salt and the basic lead salt. On concentrating the solution obtained from this purification, crystals of pure leucine were obtained. These crystals formed in pearly scales, which somewhat resemble cholesterin. When dry the crystals were light, had a satiny glossy appearance, and were not easily wet again with water. They were extremely soluble in hot water and quite easily soluble in cold water. Leucine was further identified by the fact that it sublimed, and by the crystalline form and solubility of the copper salt, and by its two color reactions with quinone, red with a solution of leucine and quinone and violet when in addition sodium carbonate was used.

Tyrosine.—The methyl alcohol solution of the copper salts was evaporated to dryness, and the residue taken up in water. The copper was removed with hydrogen sulphide and the solution was boiled with animal charcoal. After filtering, the solution was concentrated and long thin silky needles began to separate. These needles, which closely resembled tyrosine, were filtered off, and the filtrate further concentrated, when another crop of needles was obtained. These were filtered off and added to the first fraction and were then extracted with boiling 70 per cent alcohol. The crystalline residue was recrystallized from water a number of times and dried on a porous plate. This compound crystallized in the stellate groups of long slender silky needles which are characteristic of tyrosine. These crystals were relatively insoluble in cold water, very insoluble in cold 90 per cent alcohol, easily soluble in hot water, and were tasteless, colorless and infusible. The compound was further identified as tyrosine by the formation of the copper salt, which was rather insoluble in cold water and fairly easily soluble in hot water, by the fact that a solution of the compound gave a red color when boiled with Millon's reagent, and that a sulphuric acid prepared from the compound gave a violet color with ferric chloride.

Purine Bases.—Five pounds of base goods were boiled up with 10 liters of water, filtered, neutralized and concentrated to a volume of about 2,500 c.c. The solution was made strongly alkaline with sodium hydroxide and the purine bases were precipitated with Fehling's solution and dextrose according to the method of Balke. The supernatant liquid was decanted from the copper precipitate and this was washed, until free from alkali, with a solution of sodium acetate, by repeated decantations. The precipitate was filtered, freed from sodium acetate by washing with alcohol, and the copper removed by suspending the precipitate in water and treating it with hydrogen sulphide. After filtering off the copper sulphide the solution was concentrated and the purine bases reprecipitated by means of a solution of silver nitrate and ammonia. After washing with water the silver precipitate was boiled with 10 c.c. of nitric acid, specific gravity 1.1, and filtered. From this solution, on cooling and standing, crystals were deposited which were filtered off.

The filtrate was diluted with water, made alkaline by the addition of ammonia, and a solution of silver nitrate added. No precipitate was formed, showing absence of xanthine.

Guanine.—The precipitate from the nitric acid solution was washed with water, suspended in water, and decomposed with hydrogen sulphide. The solution was filtered and concentrated to about 10 c.c. when strong ammonia was added, producing a white gelatinous precipitate which was filtered off and washed with a little cold water. The precipitate was dissolved in a little warm hydrochloric acid and tested for the presence of guanine by means of the xanthine reaction and Weidel's test, both of which were positive. From the remainder of the solution the characteristic picrate of guanine described by Capranica and the dichromate described by Wulff were prepared. The method of obtaining this base, its solubility in water, ammonium hydroxide, and hydrochloric acid, the solubility of the silver salt in nitric acid, specific gravity 1.1, the color reactions, and the formation of the two characteristic salts, the picrate and dichromate, are sufficient to establish the identity of the compound as guanine.

Hypoxanthine.—The filtrate from the ammonia precipitation of guanine was boiled to expel all the ammonia and to a portion of the solution a solution of picric acid was added, but no precipitate was immediately formed, showing the absence of adenine. To another portion of the solution hydrochloric acid was added and the solution was concentrated when crystals resembling those of hypoxanthine hydrochloric separated out in whetstonelike crystals or bunches of prisms. Hypoxanthine forms a characteristic silver nitrate salt and a characteristic silver picrate salt, both of which are crystalline and relatively insoluble in water. Hypoxanthine does not give the xanthine reaction but when treated with nitric acid and bromine water a yellow color is produced which on addition of sodium hydroxide turns red, and on heating acts like the xanthine reaction. By means of these reactions the substance was identified as hypoxanthine.

THE CHEMICAL CHANGES INVOLVED IN PROCESSING.

The compounds which were isolated from the base goods are tabulated in Table IV according to the sources from which they have been derived and the chemical groups to which they belong. While it was not possible to isolate these compounds in a strictly quantitative manner, nevertheless it was evident that the purine bases were present in exceedingly small quantities, although the method used in their isolation was subject to no more error than some other of the isolation methods; this would indicate that the nitrogen of the purine bases makes up but a small percentage of the total nitrogen present in the fertilizer.

TABLE IV.—ORGANIC COMPOUNDS ISOLATED FROM SAMPLE OF BASE GOODS.

Compound.	Chemical Group.	Source of Compound.
Arginine	Diamino acids or hexone bases	Products of protein hydrolysis by acid treatment of raw materials.
Histidine		
Lysine		
Leucine	Monoamino acids	
Tyrosine		
Guanine	Purine base	Plant constituent, or product of hydrolysis of nucleoprotein.
Hypoxanthine	Purine base	Plant constituent, or product of conversion of nucleoprotein-base.

Purine Bases.—It will be noticed that the two purine bases are listed in the table as coming from different sources. It is a well-known fact that the purine bases may exist in plant tissues and plant extracts as such; that is, they are not linked up in more complex compounds in such a way that their peculiar chemical identity is lost. In the garbage which has entered into the manufacture of the fertilizer there were doubtless many sorts of plants or plant remains which contained some or all of the purine bases, and this fact alone would account for the presence of hypoxanthine and guanine in the finished product. This, however, is not the only source of the purine bases. Levene and his associates have demonstrated that some of the purines enter into the composition of the nucleic acids, which are decomposition products of nucleoprotein and that they may be obtained by a process of hydrolysis from these nucleic acids. Of the four purine bases commonly encountered, only guanine and adenine have been found to be constituent parts of the nucleic acid molecule, it matters not whether the nucleic acid be a decomposition product of animal or plant nucleoproteins. But it has been shown that the two purines found in the nucleic acids may be changed, both by chemical and biochmeical agencies, into the two other purine bases, xanthine and hypoxanthine, so that these are frequently encountered. Thus by the treatment of guanine with nitrous acid, Fischer changed it into xanthine and in the same manner Kossel changed adenine into hypoxanthine. Furthermore, Schittenhelm and Schröter have shown that the putrifactive bacteria, especially the colon bacillus, were able to convert adenine and guanine into hypoxanthine and xanthine. They also show that the bacteria have the power of splitting the nucleic acid itself. This same change is also brought about by the action of certain enzymes, such as erepsin, on nucleic acid.

With these facts at hand it is possible to draw the following conclusions as to the source of the two purine bases in this fertilizer: The guanine and hypoxanthine may be derived from plant remains which originally contained these two compounds; the guanine may arise by the acid hydrolysis of certain vegetable or animal nucleoproteins which were present in the original materials; and the hypoxanthine may have been formed by the processes of natural decomposition, such as the action of bacteria and enzymes, which had taken place in the crude materials before they were subjected to the acidulation process or during the process itself. It is not improbable that the guanine and hypoxanthine come from all of these sources.

Diamino Acids.—Of the three diamino acids lysine was obtained in much the largest amount, arginine next, and histidine in the smallest amount. These compounds are products of protein hydrolysis by acids, but may also be produced under certain conditions by the action of bacteria. Since one or more of the diamino acids have been found to be present in every protein so far examined, and since the method for the analysis and the isolation of these bases is almost quantitative, the determination of the number and amounts of the diamino acids present in a mixture of protein hydrolysis products is of importance in deciding the nature and character of the original material which entered into the processed goods.

Monoamino Acids.—Although leucine and tyrosine, which are protein decomposition products, were found in about the same quantities, the methods of isolation were so far from being quantitative that this relationship is of no significance. The isolation and identification of the other monoamino acids from the complex products of protein hydrolysis can only be accomplished, in the majority of cases, by means of the esterification method of Emil Fischer. This method is not a strictly quantitative one and requires large amounts of materials for a successful separation, and consequently was not used in this investigation. The use of methods other than that of esterification failed to isolate any other monoamino acid in quantities large enough for identification. As will be shown later, a number of monoamino acids besides the two isolated must be present in the processed goods.

Establishing the presence of these products of acid hydrolysis of proteins, namely, the diamino acids, arginine, lysine, and histidine, and the two monoamino acids, leucine and tyrosine, in the amounts in which they were found is of itself sufficient evidence to demonstrate that by the acid treatment of the crude materials used in the manufacture of the base goods the proteins contained therein have been changed. This change is shown to be a deep-seated one, since five of the compounds which are known to be final products of protein hydrolysis by acids are found. This, however, cannot be taken to mean that the proteins have been completely hydrolysed by the acid treatment, since it is possible to have present in the product of partial hydrolysis of proteins not only the diamino and monoamino acids, but also such intermediate compounds as polypeptids, peptones, proteoses, etc.

In this connection the results obtained by use of the Van Slyke method, which are given in Table V are of particular interest. As has been already stated, the base goods were extracted (1) with boiling water and (2) with boiling acid. In the former case only slight further hydrolysis of the materials in the base goods is to be expected since the free acids in the fertilizer is extremely weak, and the boiling temperature, 100° C., is that which was reached in the process of manufacture. In the case of the second extract complete hydrolysis of all the proteins or proteinlike materials is certainly to be expected, since in addition to the original hydrolysis the material was boiled with strong hydrochloric acid for 24 hours, which treatment in the case of most proteins is sufficient for complete hydrolysis. The differences in the results obtained from the analyses of the two extracts may, therefore, be expected to throw some light on the question of completeness of hydrolysis of the original proteins by the acid processing.

First it will be noticed that total soluble nitrogen in the hydrochloric acid extract is 88.64 per cent of the total N, while that of the water extract is 85.24 per cent, showing a difference of 3.4 per cent soluble N produced by further hydrolysis of the materials in the base goods. Correspondingly there is a decrease of insoluble N. There is an increase of 0.47 per cent amide N in the hydrochloric acid extract over that in the water extract. This is due to the splitting off of ammonia from some nitrogenous compounds by the hydrochloric acid and suggests the presence of some product of partial protein hydrolysis in the fertilizer which contains an acid amide linkage.

TABLE V.—NITROGEN FORMS AS DETERMINED BY THE VAN SLYKE METHOD.

Form of Nitrogen.	% of base goods H_2O ext.	 HCl ext.	% of total N in base goods H_2O ext.	 HCl ext.
Total N	1.610	1.610	.....	.....
Total soluble N	1.372	1.435	85.24	88.64
Total insoluble N	.238	.175	14.76	11.36
Amide N	.374	.382	23.23	23.70
Humin N	.031	.074	1.95	4.61
Diamino acid fraction:				
Arginine N	.111	.104	6.89	6.46
Histidine N	.117	.070	7.26	4.38
Lysine N	.081	.117	5.06	7.26
Monoamino acid fraction:				
Amino N	.543	.546	33.75	33.92
Nonamino N	.114	.113	7.10	8.27

The statement has already been made that nitrogenous compounds other than arginine, histidine, and lysine are included under the figures given for these compounds in the table. This is due to the fact that the phosphotungstic acid which is used as a precipitant of the diamino acids also precipitates peptones, proteoses, etc., as well as the purine bases, cystine, and possibly other compounds. Since nitrogen compounds other than proteins existing in the original material and susceptible to decomposition with hot acid, would have been already broken up in the processing, it follows that the changes produced by further boiling with acid would result from peptones, proteoses, etc. The difference noted between the results obtained from the two extracts for the diamino acids are therefore due to some interfering substances of the nature of proteins and not to such substances as the purines or cystine. Moreover, the latter compounds will produce the same relative error in analysis in the case of both extracts.

Of the diamino acids the only one determined directly is arginine. Its determination depends on the fact that when arginine is boiled for some time with strong potassium hydroxide, half of the nitrogen of the arginine is split off as ammonia. However, if cystine is present 18 per cent of its nitrogen is evolved as ammonia, together with the arginine nitrogen. As has already been stated, this figure should be the same for the two extracts providing that there is present in the base goods no substance precipitated by phosphotungstic acid, and giving off ammonia when boiled with strong alkali or strong hydrochloric acid. A comparison of the results obtained for arginine in the two extracts shows that the figure for arginine in the water extract is higher than that of the hydrochloric acid extract by 0.43. In other words, there appear to be present in the diamino acid fraction compounds which on boiling with alkali give off ammonia amounting to 0.22 per cent of the total nitrogen. These compounds are broken up by the further hydrolysis with acid.

Further information may be obtained by a consideration of the figures for lysine and histidine, which are obtained not by a direct determination, but by calculation from the figures obtained for arginine N, total N in the fraction, amino N and non-amino N. Lysine contains only amino N, histidine contains one-third amino N and two-thirds non-amino N, while arginine contains one-fourth amino N and three-fourths non-amino N. Since histidine N is in a measure obtained by difference from the non-amino N and the arginine N according to formula (1) on page 40, it is evident that if there are precipitated by the phosphotungstic acid compounds which contain non-amino N other than arginine and histidine, such nitrogen will be classed as histidine N, because the arginine N is determined directly.

A comparison of the results for histidine shows that there is 2.88 per cent less N calculated as histidine in the hydrochloric acid extract than in the water extract and at the same time there is an increase in lysine N in the hydrochloric acid extract amounting to 2.20 per cent. This shows that by the hydrolysis with hydrochloric acid some substance which reacted as though it contained non-amino N has been decomposed with the formation of an almost corresponding amount of amino N. Here again the indications are that this substance is of the class of compounds related to the proteins.

This is further borne out by the fact that in the monamino acid fraction the nitrogen listed as amino N has increased in per cent 0.17 and the nitrogen as non-amino N has increased in per cent 1.17 by hydrolysis with hydrochloric acid.

A comparison of the figures for humin N shows an increase of 2.66 in the hydrochloric acid extract, but since the nature of the compounds in which this class of nitrogen exists is not understood no interpretation can be given to this figure.

Proteoses.—In order to prove the presence of some intermediate product of protein hydrolysis, which is thus indicated by analytical methods, an aqueous solution of about 2.5 pounds of base goods were made and the diamino acids were precipitated with phosphotungstic acid, in the presence of 5 per cent sulphuric acid. The precipitate which formed was allowed to stand over night and after filtering off it was washed well with 5 per cent sulphuric acid. The precipitate was dissolvd in sodium hydroxide, the phosphotungstic acid precipitated by adding barium hydroxide solution, and after filtering the excess of barium was removed by adding sulphuric acid until a neutral reaction was obtained. Portions of this solution were tested for peptones, proteoses, etc., with the following results: The biuret test was positive; a precipitate was obtained on saturation of the solution with ammonium sulphate, or with sodium chloride; when the filtrate from the latter solution was treated with acetic acid a cloudy precipitation developed. Precipitates were also obtained with sulphuric acid, hydrochloric acid, phosphomolybdic acid and with phosphotungstic acid. A precipitate was formed on the addition of alcohol to the solution. This precipitate was filtered off, dissolved in dilute alkali, and on addition of very dilute copper sulphate solution the biuret reaction was again obtained. These reactions are those which are given by proteoses and by the proteins and confirm the conclusions arrived at from the results obtained with the Van Slyke method. The Millon reaction and the Hopkins-Cole reaction were both negative, showing the absence from this proteinlike compound of the tyrosine and the tryptophane radicals.

A very large number of compounds intermediary between the protein and its primary hydrolysis products may occur, depending on a great variety of conditions so that the actual identification of the compound under discussion would be a difficult matter. However, the nature of this compound may be approximately determined by the results obtained in the study of the two extracts by the Van Slyke method. These results have been already discussed and they indicate the presence in the base goods of a compound of a proteose nature, which because it gives a biuret test, must be composed of at least three amino acids. The results indicate still further that the compound is composed of acid amide radicals, diamino acids, particularly lysine, and monoamino acids, those containing amino nitrogen and especially those containing non-amino nitrogen. Since the figures obtained by the nitrogen partition method are subject to a certain amount of error when applied to such a mixture the figures can only be taken as approximate for the various forms of nitrogen which make up this compound.

The figures given for arginine in the table are probably only influenced by any cystine present. Attempts to isolate cystine from the base goods failed, although it seems unlikely that this compound can be absent. The figures for histidine and lysine are undoubtedly too high, since they include all of the other nitrogenous compounds precipitated by phosphotungstic acid, so that the absolute amount of these compounds in base goods cannot be correctly determined by this method. The figure given for the amount of amino nitrogen present as monoamino acids may be a little high, while the non-amino nitrogen figure is open to considerable error.

In Table VI are given the primary hydrolysis products of a number of proteins which may be present in the base goods. These results were obtained by the esterification method and show the different proteins vary in the nature and amount of the units composing them. Many monoamino acids, besides leucine and tyrosine, occur in these proteins, and there must consequently be present in the base goods amino acids other than the two isolated. This is apparent from the composition of the various proteins shown in the table. Owing to the large amount of amide nitrogen present in the fertilizer, which was split off by the acidulation of the original proteins of the trade wastes, it may be concluded that considerable quantities of aspartic or glutamic acids are present in this sample of base goods.

The conclusions which are to be drawn from the results obtained by the examination of this fertilizer by means of the analytical and isolation methods are as follows: The process by which the nitrogen of certain trade wastes, such as hair, leather, garbage, etc., is made more available, is recognized as a process of partial hydrolysis of the complex protein contained in such materials, resulting in ammonia, amino acids, etc., all of which are more available than the original protein material. This hydrolysis is almost complete, the nitrogenous compounds formed being principally the primary products of protein hydrolysis, together with a small amount of proteoselike compound which has not been fully decomposed.

TABLE VI.—PRODUCTS OF ACID HYDROLYSIS OF VARIOUS PROTEINS.

Compound.	"Synotin" from Cattle Flesh.	"Keratin" from Sheep's Horn.	"Keratin" from Sheep's Wool.	"Keratin" from Horse's Hair.	Halibut Muscle.	Ox Muscle.	"Legumin" from Pea.
Glycine	0.5	0.5	0.6	4.7	0.0	2.1	0.4
Alanine	4.0	1.6	4.4	1.5	(?)	3.7	2.1
Valine	.9	4.5	2.8	.9	.8	.8	...
Leucine	7.8	15.3	11.5	7.1	10.4	11.7	8.0
Isoleucine	...	....	....	...	....	....	...
Phenylalanine	2.5	1.9	....	.0	3.1	3.2	3.8
Tyrosine	2.2	3.6	2.9	3.2	2.4	2.2	1.6
Serine	...	1.1	.1	.6	(?)	(?)	.5
Cystine	...	7.5	7.3	8.0	....	....	...
Proline	3.3	3.7	4.4	3.4	3.2	5.8	3.2
Oxyproline	...	....	....	...	....	....	...
Aspartic acid	.5	2.5	2.3	.3	2.8	4.52	5.3
Glutamic acid	13.6	17.2	12.9	3.7	10.1	15.5	17.0
Tryptophane	...	....	....	...	(+)	(+)	(+)
Arginine	5.1	2.7	....	4.5	6.4	7.5	11.7
Lysine	3.3	.2	....	1.1	7.5	7.6	5.0
Histidine	2.7	....	....	.6	2.6	1.8	1.7
Ammonia	.9	....	....	...	1.4	1.1	2.1
Total	47.3	62.3	49.2	39.6	50.7	67.5	62.4

AVAILABILITY OF THE NITROGEN OF ORGANIC FERTILIZERS.

The question of the availability of the different kind of nitrogen contained in organic fertilizers is one that has caused considerable discussion. A number of methods have been proposed for determining this factor, and while some of them give helpful results, all excepting the plant method are open to more or less objection. The reason for this is that the methods are empirical and the nature of the complicated compounds in which the nitrogen is linked in the fertilizer is unknown or only guessed. When these nitrogen compounds are known and their action on plants as well as the action of the compounds which will be formed from them during their decomposition in the soil, has been determined, then the question of the availability of the nitrogen of organic fertilizers can be understood. Originally it was held that plants were only able to use nitrogen when it was offered to them in the form of nitrates; this idea, however, was modified when it was discovered that under certain conditions plants used ammonia or ammonium salts without their conversion into nitrates quite as well as they used the nitrates themselves. During the past few years it has been clearly demonstrated that plants not only use nitrogen in the form of nitrates and ammonia, but that they can also use nitrogen in the form of complex organic compounds. The action of a number of these nitrogenous compounds has been tested in this laboratory in conjunction with the three fertilizer elements and it has been found that in some cases the nitrogen compounds are not only used as a source of nitrogen for the growing plant, without any change in the compound, but that these compounds were apparently nitrate sparers; that is, the plant used them in preference to the nitrates. Instead, then, of only one kind of nitrogen compound, nitrate, or at most two, nitrate and ammonia, there appears to be a very large number of nitrogenous compounds which have properties of physiological importance to plant growth. The question of the availability of nitrogen compounds can therefore be answered only when the nitrogen compounds contained in the fertilizer can be determine in amount and at the same time classified according to their physiological action on plant growth. It is hardly necessary to state that such method does not exist at present and that the physiological action of only a part of the total number of nitrogenous compounds present in fertilizers is known.

The physiological action on plants of all of the nitrogenous compounds isolated from base goods has been determined by means of water cultures and the results obtained may be stated briefly, as follows: Both of the purine bases are used by the plant as a source of nitrogen and are beneficial to plant growth; furthermore, the hypoxanthine acts as a nitrate sparer, there being less nitrate used by the plant in the presence of hypoxanthine than when the hypoxanthine is absent. Histidine, arginine, and lysine are all beneficial to plant growth, causing nitrogen increases in the plant, and the two first diamino acids act as nitrate sparers; this may also be true of lysine, although this property of lysine has not been studied. Leucine is also beneficial to plant growth, and tyrosine, in the light of later investigations, is somewhat doubtful in action. Of the other monoamino acids which may be present in base goods, aspartic acid, glutamic acid, and glycocoll have been found to be beneficial. The action of alanine is somewhat doubtful, if apparently being beneficial in low concentrations, and the action of phenylalanine is reported as harmful. Thus we see that six of the seven compounds isolated from the base goods are actually available to plants as such and have a beneficial action. Of the monoamino acids, other than the two isolated from base goods, which have been studied in regard to their action on plant growth, three have been found to be beneficial, one doubtful, and one is reported as being harmful.

The high-grade nitrogenous fertilizers, such as dried blood, are considered to have a high availability owing to the fact that the nitrogenous materials when placed in the soil quickly undergo the process of ammonification and nitrification, the nitrogen thus being changed into a form which can be immediately used by the plant. In fact, Lipman has proposed a method for the determination of the availability of the nitrogen of organic fertilizers, depending on the amount of ammonia produced under certain conditions in a given length of time. It is evident from the above consideration that such a method does not tell the whole story, since in the decomposition of protein materials like dried blood intermediate compounds are formed which are undoubtedly in themselves beneficial to plant growth. In order, therefore, to understand the complete action of the nitrogenous materials in the base goods it is necessary to know how the compounds contained in it are acted upon by ammonifying bacteria. Jodidi has shown that the amino acids, and acid amides, are quite readily ammonified when placed in the soil, the rate of ammonia formation and the amount of ammonia formed depending apparently upon the chemical structure of the particular compound under consideration. In general, he found that the simpler the chemical structure of the nitrogen compound the more quickly and readily it was ammonified. In the light of these facts it appears that polypeptids, peptones, proteoses, and proteins would be ammonified still more slowly than the amino acids since their structure is increasingly more complex.

Hartwell and Pember in their study on the availability of the nitrogen of base goods, by means of plant tests found that it had apparently as high an availability as dried blood; the water soluble nitrogen having even a higher availability. From the nature and amounts of the compounds present in the base goods this might be predicted. In the case of the dried blood, the nitrogen is practically all in the form of complex protein material which must be broken down into simpler compounds by bacterial action, with the formation of ammonia and other nitrogenous compounds, some or all of which may be of physiological importance to plants. With the base goods the case is a little different, the greater part of the nitrogen is at once available for plant use, and at the same time these available compounds may be changed more easily and quickly by the bacteria of the soil into ammonia and nitrate, which in turn are used by the plant. The soluble nitrogen of base goods should therefore be in a more readily available form than the nitrogen of dried blood or other nitrogenous fertilizers which are entirely of a protein nature.

THE CHEMICAL PRINCIPLES UNDERLYING THE UTILIZATION OF NITROGENOUS TRADE WASTES.

In these days of conservation and scientific management more and more attention is being paid to the trade wastes from the various industries and to the municipal scrap heaps. Things which were formerly thrown away are now often made to pay for the entire cost of production. After the resources of the chemist and inventor have failed in finding any other use for some industrial waste, if it be of a nitrogenous nature, the fertilizer industry is turned to as a last resort. Here, however, all is not plain sailing, since many of these nitrogenous substances are of such a nature that the nitrogen is said to be "unavailable" for plant use, that is, the substance is of such a nature that it is not readily decomposed by the natural agencies at work in the soil, so that for the purpose of plant nutrition the nitrogen of such substances is worthless or of little value. In order to render available this type of nitrogenous material many different kinds of treatment have been suggested, and the patent literature abounds in inventions of this sort.

It has already been stated that in order that the plant may make use of the nitrogen of even high-grade organic fertilizers, it is necessary for the proteins therein to be at least partially decomposable by the biological and biochemical agencies of the soil. The low-grade organic nitrogenous fertilizers resist decomposition by these biological and biochemical soil agencies, and their nitrogen is therefore considered to be less available for plant use. The guiding idea behind the processes proposed for the treatment of trade wastes, which will not decompose easily in the soil as such, is to change the nitrogen compounds contained in them in such a way that ammonia is formed and that their decay in the soil is more rapid.

Much of the nitrogenous materials in trade wastes are of a protein nature, since the products from which these wastes are derived are either of animal or vegetable origin. Such is the case with the wastes used in the manufacture of base goods. It has been shown that by the process used in the case of this fertilizer the nonavailable nitrogenous materials have been made highly available, not only because the nitrogen compounds can be ammonified quickly in the soil, but also because these compounds are directly utilizable by plants. This change in the nature of the nitrogen compounds has been brought about by the partial hydrolysis of the proteins contained in the various trade wastes used in the manufacture of the fertilizer. When proteins decompose through natural conditions, be they in the soil or out of it, a certain amount of hydrolysis of the proteins takes place and if the decomposition is allowed to proceed long enough under proper conditions complete hydrolysis will result.

The principle involved in making the nitrogenous material in the soil available and in increasing the availability of the low-grade nitrogenous materials by factory treatment is therefore the same. In other words, the general chemical principle to be applied in making available the nitrogen of low-grade fertilizers, trade wastes, etc., is that of complete or partial hydrolysis by any suitable means of the proteins contained in the wastes. Partial hydrolysis of proteins may be accomplished by means of heat, boiling, steaming, heating under pressure, and both partial and complete hydrolysis may be obtained by treating with strong acids or alkalis, either in the cold for a long time or heating to a high temperature, the extent of hydrolysis depending on the several conditions. In a number of processes already in use various of these treatments are practiced, resulting in different degrees of hydrolysis of the original proteins. While the availability of the nitrogen of a fertilizer depends on the substances in which the nitrogen is contained, it also depends on the extent of hydrolysis of the proteins used in the manufacture. It may be stated that in general the more extended and final the hydrolysis the more available the nitrogen of the compounds formed, since, as has been shown, the final products of hydrolysis are utilized by the plant as such and are at the same time more readily changed into ammonia by bacteria, etc., than are the intermediate compounds produced by partial hydrolysis.

SUMMARY.

The base goods used as a type of processed fertilizers is an organic nitrogenous fertilizer which contains acid phosphate. This product is produced by the action of sulphuric acid on certain trade wastes; the heat is generated by the interaction of the acid with the organic wastes and rock phosphate in the course of the manufacture of acid phosphate. It is here shown that the hydrolysis of the protein is almost complete, the nitrogenous compounds in the finished fertilizer being principally the products of primary protein decomposition, together with a small amount of a proteoselike compound which has persisted.

From the sample of base goods were isolated the following nitrogenous compounds: two purine bases, guanine and hypoxanthine; the three diamino acids, arginine, histidine, and lysine; and two monoamino acids, leucine and tyrosine. A proteoselike compound was also obtained and its general nature established.

By means of the Van Slyke method the approximate proportions of the different forms of nitrogen contained in the fertilizer were estimated, and the extent of the hydrolysis of the original proteins was determined. It was also shown by this method that the proteoselike compound was composed of acid amide radicals, diamino acid radicals, especially lysine, and monoamino acid radicals, particularly the monoamino acids which contain non-amino nitrogen.

The question of the availability of nitrogen is discussed and from a consideration of the amount and the physiological action on plants of the different forms of nitrogen present in the fertilizer it is concluded that the water soluble nitrogen of this fertilizer should have an availability equal to or greater than the nitrogen of dried blood, or other high-grade fertilizers. These results are in accord with the results obtained by the plant method of determining availability.

The general chemical principle which underlies the method for rendering available the nitrogen contained in most trade wastes, which are to be used as fertilizing materials, is shown to be either partial or complete hydrolysis of the protein of the wastes by any suitable means.

The more complete the hydrolysis the more available the nitrogen in the fertilizer becomes, since the products of complete hydrolysis of proteins are not only utilized by the plants themselves as nutrients but they are more easily ammonified when placed in the soil than are the more complex compounds, such as peptones, proteoses, and the proteins themselves.

This investigation aims only at an explanation and exposition of the general chemical principles involved in the treatment of trade wastes and other organic material to render the nitrogen contained therein more available for agricultural purposes. It does not aim to present the research methods here employed as general methods for analyzing such fertilizers, nor can the quantitative figures obtained be expected to apply to all products of similar manufacture, for the reason that the different kinds of nitrogen compounds will necessarily show different proportions according to the nature of the materials which enter into the mixture.

DISCOVERY OF PHOSPHATE IN ELLISTON FIELD, MONTANA.

The discovery of rock phosphate at Melrose Mont., by H. S. Gale, of the United States Geological Survey, in October, 1910, suggested the strong possibility of its occurrence in the western part of the state. In 1911 rock phosphate was discovered by J. T. Pardee, of the Survey, at three localities in western Montana—in the Garnet range, 6 miles north of Garrison; at Philipsburg; and half a mile east of Elliston. A detailed examination of the phosphate field at Elliston was begun in 1913 by R. W. Stone and C. A. Bonine, and their report has just been published by the Geological Survey as Bulletin 580-N.

The phosphate in the south half of the Elliston field is within 2 miles of the Northern Pacific Railway and readily accessible to it. The farthest point in the northern part of the field is between 6 and 7 miles from the railway by way of Dog Creek valley, down which there is an easy grade. In the south half of the Elliston field the phosphate bed stands nearly vertical along about 2 miles of its outcrop, but near Elliston it is so faulted that an estimate of the area underlain by it is difficult. On the assumption, however, that this part of the field contains the equivalent of 3 miles of outcropping bed that could be mined to a depth of half a mile, there is in the south half of the field half a square mile underlain by phosphate; and as the few measurements in this part of the field suggest an average thickness of 4 feet, it is estimated that at least 15,204,861 tons of phosphate rock is present in the south half, while in the northern half there is an estimated deposit of 70,000,000 tons of rock, making a total of more than 85,000,000 tons in the whole Elliston field.

These deposits have not yet been developed, owing to the recency of their discovery and to the lack of markets sufficiently near to justify mining and reduction. The demand for fertilizer products in the western states is not large, owing to the lack of intensive cultivation and the newness of the agricultural lands; but there is a growing tendency to use fertilizers where the land is farmed extensively, especially in the middle west. The western phosphate deposits are favorably situated to meet a demand from this section of the country and will doubtless be utilized in the future.

METALLURGY

THE MICROSCOPIC STRUCTURE OF HIGH SPEED STEELS.

By H. B. PULSIFER.

(Continued from January Issue.)

The specimens heated to 1160°, 1210° and 1280° before quenching show a wealth of structure not to be expected by a mere perusal of the literature on the subject.

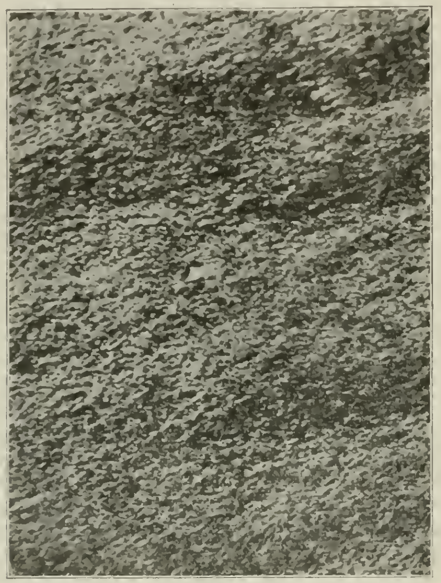

Fig. 1.

With these samples we find some instances of the hard martensitic character previously described; there are cases of the finely cellular austenitic structure, supposedly the most to be desired for hot work in the machine shop; then we find cases of striking novelty due to increased grain size, transitions between martensite and fine austenite and transitions between the two latter and an enormous grain which is characterized by an intermediate zone of apparently pearlitic nature which, for lack of better understanding, we refer to as the pearlitic fringe. A segregating of pearlite about the boundaries of the huge-grained austenite is to be seen in several specimens while in at least one instance a carbide rib cleaves such pearlitic accretions.

If we are here dealing with the most beautiful and striking forms it may also have an equally practical significance for it makes clear why manufacturers of such steels insist upon, and users also practice, the grinding off of the exterior after heating and quenching. In a way is also shown why no other treatment is so successful for developing fine cellular austenite as heating to the very highest possible, quenching, and grinding; this process giving better results than any other method of treatment yet devised.

But to consider the findings in detail before more of the general. Fig. 1 shows steel A quenched from 1160°. Its hardness is uniformly about 52 by the scleroscope; it etches readily only with sulphurous acid, when the finely granular markings of typical martensite appear as plainly seen in the print. Of all the steels this kind, alone, holds to its martensitic nature on heating and quenching. Heated to 1210° and 1280° the same result is given so no further prints of this sample A will be shown. At these higher temperatures the carbides in this steel are quite dissolved and the field is remarkably uniform and the absence of cellular austenite or transitions or zones remarkable. No clue to this unique behavior is to be found in the chemical analysis as given, nor in the treatment as recorded. Further research might contradict these results or find further explanation for this steel differing from the others.

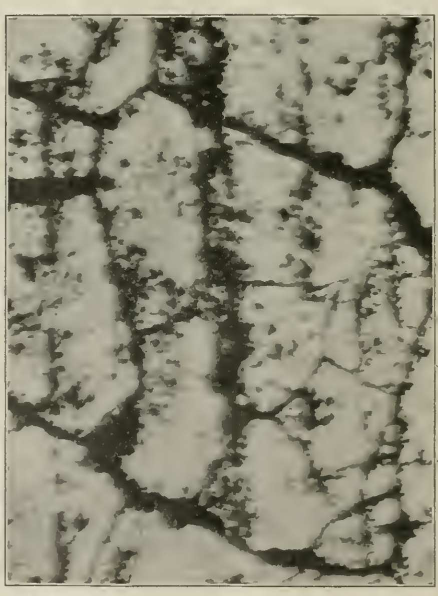

Fig. 2.

Fig. 2 shows a view of steel B as quenched from 1160°. The hardness of the prepared surface has

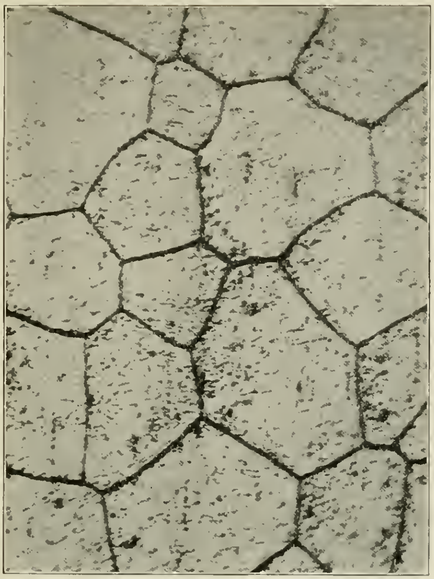

Fig. 3.

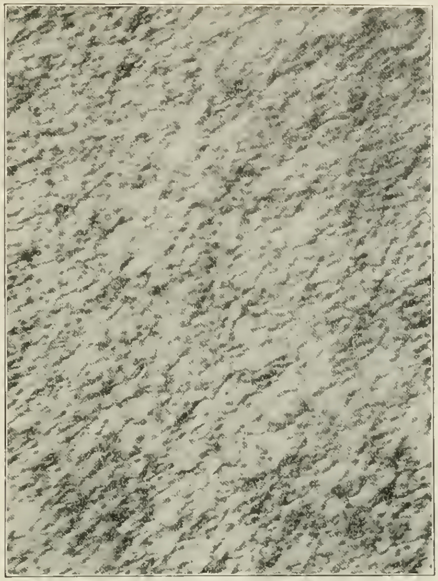

Fig. 4.

fallen to 30 or 40 on one side but is as high as 60 along one edge (this edge possibly rested on the bottom of the furnace and was not heated as high as the rest of the piece). Even sulphurous acid does not tarnish the surface to the naked eye, yet under the microscope appears the huge grain of overheated austenite. The strong etching has brought out the enormous polyhedral grains and deeply eaten into the boundaries; the difficultly attackable surface of the massive austenite is seen generally smooth and only in places of a granular texture. The sub-grain, a finer grain within the huge grains, is conspicuous and found on other samples also.

Fig. 3 shows steel C as quenched from 1160°. This particular spot indicates a slight overheating of the already perfectly formed austenite. As in the previous

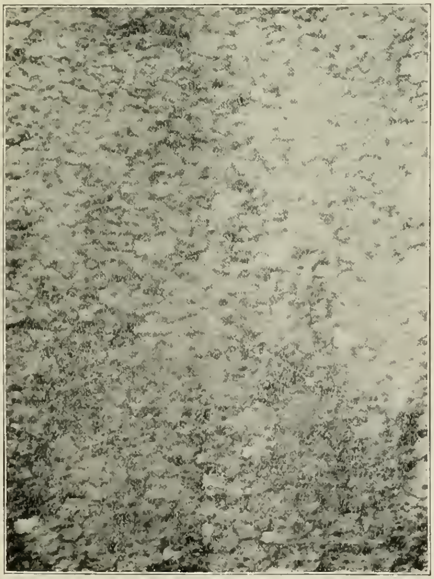

Fig. 5.

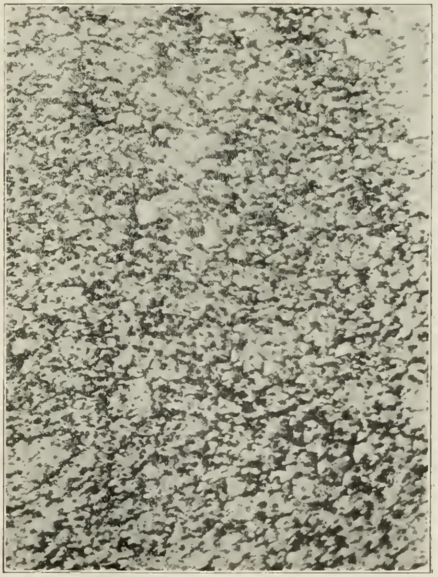

Fig. 6.

figure, no carbide droplets appear, they doubtless having been dissolved at the high temperature. Even sulphurous acid has no effect to the naked eye; the result appearing, however, under the lense. It may be stated the picric-nitric acid treatment while also unable to tarnish this sort of solid solution does rather weakly bring out the cells or grains when viewed under the microscope. It takes the sulphurous acid to strongly and sharply outline the boundaries with sharp relief. Little v-shaped pits decorate the rather smooth surface while the hardness of the material has fallen to under 40.

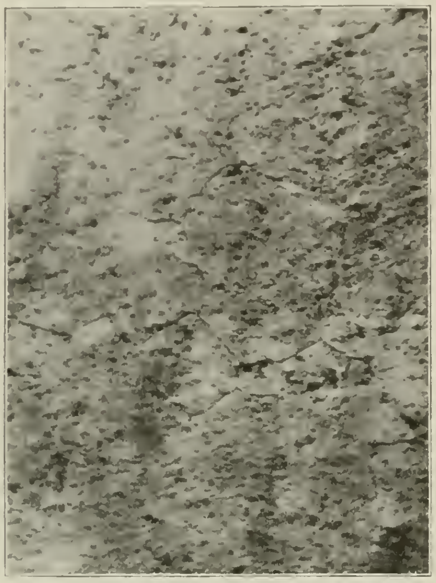
Fig. 7.

Steel D as quenched at 1160° presents no unusual departure from views as seen on other surfaces. The core of the piece is hard martensite, testing around 60, while the exterior is large-grained austenite quite similar to that seen in Fig. 3. Under the action of the acids the surface tarnishes in spots, indicating the areas of attackable martensite and the exterior of cellular austenite.

Steel E is a spotted surface as exposed by grinding after quenching at 1160°. The core is martensite with faint development of cellular lines, in places there being a noticeable segregation of what etches dark and resembles pearlitic or high-carbon spots. Hardness varies from 40 to 60.

Fig. 4 is from the surface of steel F at quenching from 1160°. The hardness is from 45 to 50; acids do not corrode to the naked eye. We plainly have a case of the first development of the austenitic structure. The grain is of the finely cellular austenite at its closest texture found in the whole series. The hardness is noticeable less than good martensite affords, the etching test indicates the absence of the colorable martensite while the print (Fig. 4) shows how the granules of martensite have smoothed out and certain of the incipient delineations of that solution are more clearly defined as the boundaries of the new grains.

Fig. 5 indicates an identically similar condition in steel B as quenched from 1210°; the hardness is around 55, the surface is only slightly browned by sulphurous acid, while the cellular grain is nicely prominent. In this print more than in the previous one, the carbide droplets are present.

Steel C, quenched at 1210°, is in the martensitic condition where exposed by the section as ground; its hardness goes up to 78 as a maximum.

Steels D and E, quenched at 1210°, are just bordering on the line between martensite and austenite. Both have high hardness, about 75, yet they etch scarcely at all and show under the lense a pronounced differentiation in the field; the former martensitic ground is now smoother and separated by the lines which a little more heat would have intensified to the clean cut grain boundaries of austenite.

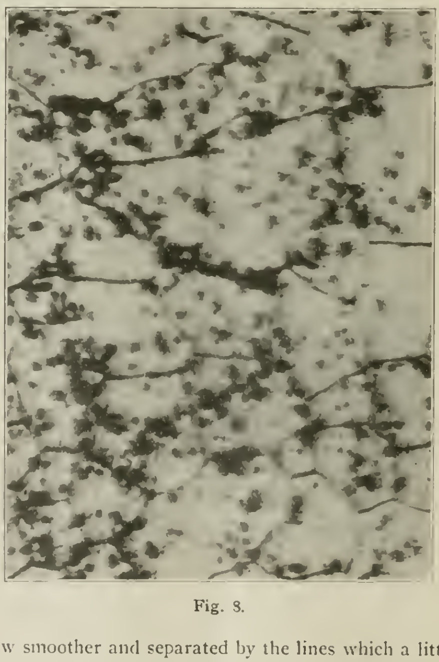
Fig. 8.

Fig. 6 is of steel F quenched at this temperature (1210°) and, although possibly a little too deeply corroded, is right at this stage which has much of the hardness of martensite with an unquestionable prominence of cellular grain. Steel F is from 54 to 61 hard on the scale: as seen in Fig. 6 it is partly like martensite, partly like austenite, and not wholly characteristic of either. This is one of the most valuable properties of the high-speed steels: they afford an unsurpassed series of gradations between these two solid solutions which we commonly designate as martensite and austenite.

Fig. 7 shows steel C quenched from 1280°. Here we have another sort of intermediate condition between martensite and austenite; large-grained austenite is evidently taking shape in massive martensite if the grain is any criterion of the more fundamental nature. This specimen shows spots of this sort surrounded by huge austenitic grain; these spots are some 64 hard while the periphery may be as soft as 40. Needless to say, few such interesting gradations came to notice. Much of the central core area showed absolutely no traces of such cellular beginnings while other spots, likewise rough and somewhat tarnishable, displayed even further extension of the grain separation.

Steel D as quenched from 1280° has a fine austenitic core quite like Figs. 4, 5 and 6 while the outside is coarse and much like Fig. 3. The harder localities run up to 74 while the coarse austenite is only some 40 by the test.

Steels B and F probably had some mistake in quenching or numbering for they are soft and appear to have pearlitic nature, quite out of accord with what all the other specimens indicate as the right nature for this sort of steel as quenched at temperatures above 1000° C.

Fig. 8 shows steel E as quenched from 1280°. Hardness is from 32 to 42 and the acids leave the surface bright and polished to appear as in the print under the microscope. The polyhedral grain is strongly developed to medium size by the high temperature, while the pits are largely segregated about the boundaries of the grains. This pitting has before received notice; it is apparently a localization of impurities, probably chiefly carbon. In the next and final installment prints will be shown which show this segregation further completed. This print is valuable as indicating an intermediate stage with most of the pits along the boundaries although plenty are yet inside the grains.

In presenting the results of our inspection of the samples it must be plainly understood that no attempt has been made to afford an exhaustive summary of every normal or abnormal condition, or how a complete section through each specimen should appear. When the samples were ground the rough exterior was removed and then a suitable surface shaped as quickly as convenient; sometimes the final section came rather near the original exterior, sometimes it happened to get deeper through inability to get a p[illegible] without considerable grinding. From this it is apparent that sometimes about the entire surface would lay in the coarsely granular austenite of the exterior, sometimes the section would lay in an intermediate zone, sometimes the section be through the quite uniform and main central core. In a way this haphazard slicing of the specimens has afforded a profuse display of the structures; a more systematic or a continued research would demand that the specimens be ground to afford a section through the very center axis of each piece. The pieces should also be equally heated on all sides, not laid on the hearth floor.

With attention to these necessary details and even more precision in numbering, heating and quenching a certain correlation of temperature, time and structure might be obtained. What has been afforded, however, we believe indicates an excellent series of normal and oversize grain.

With the concluding prints of other large grain structures and other transition appearances it is hoped that the prints will prove not only interesting for their own account but illuminating through their bearing on practical operations.

MANGANESE.

By THOMAS OSBORNE.

Manganese is an important mineral due to its use in the manufacture of iron-manganese alloys, such as spiegeleisen, ferromanganese and siliconmanganese; the two former are extensively used in the manufacture of steel, as reducers and recarburizers. A large quantity of high grade manganese ore is also used as a depolarizer in the manufacture of dry-cell electric batteries. Manganese is therefore one of the more interesting and important of the minor metals. Manganese steel has special qualities to recommend it; it is extremely hard, but not brittle, it is malleable, though it offers considerable resistance to cutting tools. These properties make manganese steel extremely useful for the manufacture of such articles as gears, pinions, railroad switches and the digging parts of crushing machinery. For the production of some of these articles manganese is practically the only alloy available. Manganese bronze is produced by alloying manganese with copper, and silver bronze is obtained by alloying manganese with aluminum, zinc and copper. Oxides of manganese are used in glass manufacture; as a drier of varnishes and paints; in dry batteries; in the production of certain disinfectants; also as a coloring material for staining glass, pottery and tiles. There are many other uses for this important mineral.

In the United States at some of the mines, the ores are treated and alloys produced, such as ferromanganese and spiegeleisen, in very large quantities; thus during 1913 the output amounted to 227,900 tons, an increase of nearly 50,000 tons over the output of 1911. Some of the richest deposits of manganese ore are located in the Russian Caucasus.

Since the construction of the Transcaucasian railway the output of ore is very great and is exported in all directions; large quantities are sent to the United States, Great Britain, Germany, France and Belgium.

For the time being the war has completely cut off this supply. Considerable quantities of manganese ore are produced in New Brunswick, and Nova Scotia; Quebec and Ontario have smaller deposits.

The Nombre de Dios manganese-bearing region of Panama is reported to cover an area of nearly 300 square miles along the Caribbean sea. The ores there occur as oxides, principally psilomelane, but also pyrolusite and brannite; the output has been exported for over 40 years. Manganese ores are also very extensively distributed in Brazil. In Chili the manganese deposits are all on the west slopes of the Andes mountains. Carbonates, silicates and oxides occur in Spain. Manganiferous iron ores are found in Belgium, also associated with hematite. Within the German empire there are very extensive deposits. Three types of manganese ores: pyrolusite with manganite, hausmannite with brannite, and carbonite and silicate of manganese accompanied with iron ores occur in Sweden. But the largest producer in the world is Russia, it has held that position for many years and has deposits in both Asiatic and European provinces. In both Asia and Africa manganese ores are produced in areas as far apart as Cape Colony, the Sinai peninsula, India, Java, Borneo, the Philippine islands and Japan.

THE WORLD'S OUTPUT.

The total production of manganese ore throughout the world ranges from 2,000,000 to 2,300,000 tons, of which about 49 per cent comes from Russia. The output is distributed as follows according to the most recently available figures:

Russia	987,700 tons	Spain	16,600 tons
India	674,300 tons	Turkey	14,100 tons
Brazil	163,500 tons	Japan	11,000 tons
Germany	75,700 tons	Greece	10,400 tons
Austria-Hungary	28,100 tons		

Other countries have smaller outputs. Russia as the larger producer placed an embargo on the export, shortly after Great Britain declared war, but it has since been removed, as it is inoperative through the closing of the Black Sea and in consequence of the output of so many other countries, all of which are able to increase their production to the detriment of Russia after peace has been re-established. Great Britain exports large quantities of ferromanganese to the United States; American steel makers depend mainly on that supply; the outbreak of war caused considerable anxiety, also rumors that the British government might prohibit the exportation of ferromanganese. As there are reported to be ample supplies in Germany, a British declaration of contraband would seriously embarrass American industry, without answering any useful purpose. A temporary shortage will tend to develop the Brazil output; manganiferous iron ores are being opened up in California, so that with enterprise America may be rendered quite independent of the rest of the world. The Brazilian ore is of exceptional excellence, principally pyrolusite and rhodonite. The deposits have been described as immense, more than ample to supply the whole world for the next fifty years; they occur in the vicinity of Corumbo; in the states of Minas Geraes, Bahia, Matto Grosso, Parana and Santa Catharina.

In addition to manganiferous ores there are several other sources of supply such as manganiferous iron and silver; as well as the manganiferous residuum from zinc roasting. In the United States there are many deposits, but only in a few places do they occur in sufficient quantity to be of sufficient commercial value. They have not yet been systematically developed, as supplies could be so readily imported. The war will now give an impetus, which may have far reaching results in the early future.

Deposits occur in the New England, Appalachian and Piedmont regions in the eastern United States; also to an unknown, but probably extensive extent, in central western California. Manganiferous iron and silver ores are also widely distributed.

The use of manganese for a variety of purposes is of great antiquity, there cane be no doubt that it was well known at least as long ago as the time of the ancient Egyptians. One of its first uses was in glass making. Egyptian and Roman glasswares have been shown by analysis to contain over two per cent of manganese oxide. Pliny mentions the use by the Romans of manganese oxide under the name of magnes, for discoloring glass; he considered it a variety of lodestone, or magnetic iron ore. The value of manganese as a deoxidizing and solidfying agent in the manufacture of steel was discovered in the early years of the last century. Manganese steel has been used in a variety of ways in the works of the Panama Canal, where two manganese steel dippers of 10 cubic yards' capacity and weighing approximately 37,000 lbs. each are used on two large dredgers, the Paraiso and the Gamboa. A rapid determination of manganese in the presence of iron is as follows: The solution containing iron and manganese is precipitated whilst boiling by an excess of sodium hydroxide and about 1 gramme of sodium persulphate. The precipitate is then washed by decantation and then on a crimped filter until the washings are neutral. The wet filter and the precipitate are then introduced into a long necked flask of 200 to 250 ccms. capacity, then 20 ccms. of hydrochloric acid added and the flask closed with a ground stopper fitted with absorption bulbs and a capilliary tube extending to the bottom of the flask. The bulbs contain 3 gms. of potassium iodide and 5 gms. of sodium acetate in solution and 4 to 5 gms. of zinc oxide in suspension. The solution in the flask is boiled while a slow current of carbon dioxide is passed through. When the manganese present is only small in amount, the chlorine liberated by the manganese dioxide is all evolved in two or three minutes. The liberated iodine in the bulbs is titrated with an N/10 solution of sodium thiosulphate. A blank test should be made on the reagents. Experience has shown that this method yields very accurate results.

Manganese forms part of about 100 minerals and is relatively a widespread element, but practically all the manganese of commerce is derived from material containing one or more of the minerals polianite, pyrosulite, psilomelane, wad, manganite, braunite, and franklinite. Commercial manganese ores are those which contain approximately 35 per cent, or more, of manganese, and otherwise conform to the specifications of the trades in which they are used. The composition and percentage of the more important manganese ores are as follows:

Mineral.	Composition.	Manganese Percentage.
Polianite	MnO_2	63.2
Pyrolusite	$MnO_2 nH_2O$	60-63
Psilomelane	$MnO_2 (MnKBa) OnH_2O$	45-60
Wad	Hydrous impure mixture of manganese oxides	Variable
Manganite	$Mn_2 O_3 H_2O$	62.4
Braunite	$3Mn_2 O_3 MnO . SiO_2$	69
Franklinite	$(Fe Zn Mn) O (Fe Mn)_2 O_3$	Variable
Rhodochrosite	MnO, CO_2	47.56
Rhodonite (manganese pyroxene)	$Mn O Si O_2$	41.9
Tephroite	$2Mn O . Si O_2$ (manganese olivine.)	54.3
Spessartite	$3MnO . Al_2 O_3 . SiO_2$ (manganese garnet.)	33.3

These minerals are found either separately, or combined among themselves, or with other minerals; they form four different classes of materials from which manganese can be obtained commercially: (1) manganese ores; (2) manganiferous iron ores; (3) manganiferous silver ores, and (4) manganiferous zinc ores. *Manganese ores* consist of various mixtures of manganese oxides sometimes containing admixtures of manganese carbonate. *Manganiferous iron ores* consist of mixtures of manganese and iron oxides. *Manganiferous silver ores* consist of mixtures of manganese and iron oxides with small quantities of silver sulphide and lead carbonate. As a rule the iron content exceeds the manganese content, but locally the iron is sometimes altogether absent. Manganiferous silver ores are divided into three classes according to their uses: (1) The greater portion of the manganiferous silver ores are used for their silver and their lead contents. Manganese and iron content often insures those ores obtaining a higher price on account of their fluxing value. (2) A second class of maganiferous silver is too low in silver and lead to be used as a source for these metals, but is sufficiently high in manganese and iron to be used for the manufacture of ferromaganese and of spiegeleisen, as is the case with the high grade manganiferous iron ores mentioned above. (3) There is a third class of manganiferous silver ore too low in silver and lead to be used primarily for these metals and too low in iron and manganese to be used for the manufacture of iron-manganese alloys. This ore is sold to the smelters as flux, the iron and manganese become waste products, while the silver and lead contents are recovered during the smelting. *Manganiferous zinc residuum* is an artificial furnace product consisting of mixtures of manganese and iron oxides in a matrix of slag. Manganiferous zinc residuum is obtained from zinc volatilizing and oxidizing furnaces, using special zinc ores; the residuum consists largely of iron and manganese oxides, the zinc having been removed by volatilization and collected as zinc oxide.

AN EXAMPLE OF THE DEVELOPMENT OF HEAT TREATMENT.[*]

By ROBERT R. ABBOTT.[†]

In the early days of the automobile no one was critical; starting the engine and keeping it running occupied most of the driver's spare moments and the detail of a broken gear or twisted shaft was of minor importance. If hardened gears were used a little distortion would not be objectionable, rather otherwise, because the noise caused by them was welcome as nobody wanted a car whose coming could not be heard.

The manufacturer had not much choice in his selection of steel. If he wanted hardened gears or bushings he had a choice of two things, one was to use tool steel and the other was to use a low carbon stock, which would be surface hardened after it was machined. The low carbon stock available for this purpose was of two kinds, bessemer or open hearth, the former usually known in the shop as screw stock and the latter as machinery steel. For hardening these steels two processes were used, first, cyaniding and second, carbonizing or pack hardening. In the first process the part was usually dipped in a pot of melted cyanide of potassium and when heated through to a temperature of about 1450° F. it was quenched in water. In the pack hardening method the parts were packed in cast iron boxes or pipe with ground up bone or charred leather, and heated in a furnace to a temperature of from 1600 to 1900° for several hours, depending upon the depth required and were then either allowed to cool down in the carbonizing boxes, reheated and hardened the same as tool steel, or were quenched directly from the carbonizing boxes. The use of tool steel gears was rare as the cost of machining the high carbon steel was excessive.

As the industry developed from the experimental stage the machines became heavier, and the engine more powerful, both of which caused a higher stress to be placed upon the various steel parts, breakages became more frequent; for the tortioned parts, front axles, steering parts, etc., this could be met by increasing their size; for the gears this remedy could not always be successfully applied for various practical reasons. At this time very little attention was paid to the chemical analysis of the material. The manufacturer, however, soon realized that the analysis of the steel had a vital bearing upon his product, his brittle transmission gear he found usually to be high in carbon and as a result he tried to obtain a low carbon steel for carbonized parts. As the business developed and the demand became greater for better material a few of the steel mills began producing special steel for the automobile trade. These generally consisted of a low carbon steel for carbonizing and a medium carbon steel for shafts; the first usually containing .20 to .30 percent carbon and the latter .30 to .40 percent. The fact that the analysis was kept fairly uniform gave a uniform product and was a distinct advance. The next step was the development of alloy steels. A plain carbon steel of .25 percent carbon has a tensile strength of about 60,000 lbs. per sq. inch. If 3 percent to 5 percent nickel is added to this its strength will be about 80,000 lbs. per sq. in. These alloy steels were produced of various types and for various purposes. The nickel steel usually contained 3½ percent nickel with carbon contents varying from .10 per cent to .50 per cent. The lower carbons, say below .25 percent, being intended for carbonized parts, principally gears, the medium carbons, between .20 to .35 being used for forged parts such as steering knuckles, arms, front axles, etc., while the higher carbons, from .30 to .50 percent, were used for tortional parts, and in some cases for gears which were not carbonized. Chrome and chrome vanadium steels were produced; the chrome steels were usually used in ball bearings and contained about 1.00 percent carbon and 1.00 percent chrome; the chrome vanadium steels had carbon contents similar to the nickel steels and with about 1.00 percent chrome and .20 percent vanadium. Chrome nickel steel of various types was used; it could be roughly classified into two types one containing 3½ percent nickel and 1½ percent chrome and the other with 2 percent nickel and 1 percent chrome. These chrome-nickel steels were largely used for gears and contained about .50 percent carbon. They were hardened in oil without carbonizing. Silicon steels were produced containing from 1.00 to 2.00 percent silicon and about .50 per cent carbon. They were used for gears in a manner similar to the chrome-nickel steel and also for springs.

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The use of these alloy steels determined the difference between success or failure for many automobile firms. Practically coincident with their development came the development of heat treatment. While the use of alloy steel was a great forward step, still the tendency was to produce more powerful motors and at the same time lighter weight cars; it soon became evident that steel with tensile strength of 150,000 to 200,000 lbs. per sq. inch was required and still a high degree of toughness was essential; heat treatment alone could supply this.

We will consider briefly the evolution of the above process by following a development of the material and treatment used in the manufacture of gears. These form a very essential part of the automobile; in the transmission, in driving the rear axle and in the differential they are subjected to the greatest stress. Originally many of these were cyanided. In this method of hardening a thin film of high carbon is produced on the surface by the melted cyanide of potassium and upon quenching the surface is hardened; the depth of this surface is rarely over .005″.

In transmitting power through gears practically the entire load comes upon a line across the gear tooth; considering a section through a tooth it is readily seen that we have a beam with a load at a single point, this will cause a deflection at this point and unless the thickness of the beam of high carbon is sufficient to prevent the deflection going beyond the elastic limit slight fractures will occur; these fractures will rapidly multiply and minute particles will become detached from the surface which will rapidly wear away.

In the carbonizing process the hardened shell can be made as deep as desired; for ordinary automobile gears this depth varies from .01 in. to about .06 in. The percentage of carbon in the surface can be varied. It should run above 1.10 percent and preferably between 1.25 per cent and 1.50 per cent; this grades down in steps until the core is reached with the percentage of carbon of the original steel.

A steel containing about .9 per cent carbon is composed of an intimate mixture of pure iron and a carbide of iron known as cementite. This mixture is called pearlite.

A steel containing more carbon than .9 per cent has an excess of cementite above that necessary to form the pearlite; this cementite exists as sheets or as a network in the pearlite. A steel containing less than .9 per cent carbon has an excess of iron surrounding the pearlite. In such a steel containing a fairly high per cent of carbon, say .8 per cent the iron exists as a network similar to the cementite of the 1.10 per cent carbon steel above; in a lower carbon steel the pearlite forms grains in a mass of iron. A steel containing nothing but pearlite is known as a saturated steel and one containing an excess of iron is an undersaturated steel.

When a piece of plain carbon steel has been hardened at the lowest temperature at which it will harden, namely, 1375-1400°, the pearlite changes from a mechanical mixture to a solid solution; this solution is known as martensite and is shown in figure 3 magnified 800 diameters.

Any excess cementite above that originally necessary to form the pearlite will be unchanged by this hardening process. Also any iron in the under-saturated parts will remain unchanged.

In a piece of carbonized steel containing say 1.10 per cent carbon in the surface and having originally .20 per cent carbon we will have after hardening at the lowest possible temperature three zones of different structure (a) the outer surface will consist of martensite traversed by a network or sheets of cementite; (b) below there will be a zone of pure martensite; this will grade into, (c) core which will consist of a ground mass of iron with martensite grains in it.

Now a piece of steel which has been hardened in this way is extremely brittle. On first thought it would seem as if the soft low carbon core should give toughness to the piece even if the outer shell was hard. For various reasons which are too lengthy to consider here this is not so unless the area of the core is very large compared to that of the case and unless it also contains a comparatively low carbon content. One of the important causes of the brittleness is, however, the presence of the cementite. Cementite is extremely hard; it is harder than martensite which is the principle constituent of hardened steel. It is, however, very brittle and a sudden shock or too great a strain will cause it to fracture. When it exists as a net or as sheets or needles this fracture extends for a considerable distance and frequently does not stop at the end of the cementite but is carried right through the soft core causing a complete break. Another objectional feature about the cementite in this connection is the fact that in the surface of a gear tooth where a high unit pressure occurs, minute fractures will occur in it which will cause the surface to spawl or chip off. This is a very common occurrence.

This lack of toughness in a carbonized gear tooth led to considerable of the development of alloy steels and their heat treatment. Many gears were made of chrome nickel and silicon steels containing about .50 per cent carbon and were oil quenched and drawn without carbonizing. The carbon was low enough so that no cementite was present. The alloy gave an extremely strong tooth; the cost of machining was higher than for a low carbon steel. Such a surface would not wear as well as one containing a higher percentage of carbon. A marked step in advance was then made in the development of the so-called double treatment of carbonized parts; this is applied to either a plain or an alloy steel.

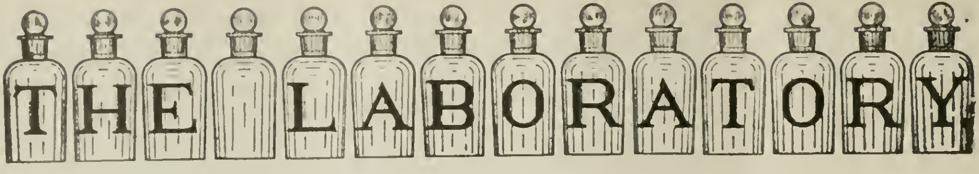
We have seen that when a piece of carbonized steel is hardened at the ordinary hardening temperature we have present 3 different zones. Now if a temperature higher than the hardening temperature is used it will be found that the excess substance in the inner and outer zones, namely, iron and cementite, becomes less in amount while the martensite becomes greater; briefly the martensite absorbs both the iron and cementite. As the temperature is raised still further this absorption continues until finally all three zones contain martensite alone The temperature at which the last of the cementite is absorbed will usually be different from that at which the last iron goes into solution; also the time element for the absorption of the cementite is much greater than for the iron. The temperature of final absorption of the iron increases as the amount of iron originally present in the core decreases. Also the temperature of final absorption of the cementite is higher as the temperature at which the original carbonizing took place is higher. This temperature can also be changed by suitable selection of the material with which the carbonizing is done.

In general all the above factors are adjusted so that the temperature of final absorption of the iron shall be higher than that for the cementite, if this is not done. A triple treatment must be used to obtain maximum results. This will not be considered here. If the steel is now quenched from above this temperature, we have martensite throughout. There is a difference in the physical characteristics of the martensite formed in the three original zones; that in the center zone will be fine grained, while that in the middle and outer will be very coarse. Steel treated in this way will be less brittle than when at the lower hardening temperature, but it will not wear so well because the cementite is no longer present and this is the hardest constituent formed in steel. If the steel is now reheated to the regular hardening temperature, i. e., 1,375 to 1,400, and then quenched we find an enormous increase in toughness and also in hardness and wear resisting ability.

Comparing these structures to the corresponding ones produced by single quenching it will be seen that both zones contain the same constituents and in the same relative proportions. However, the structure is entirely different, the cementite in the outer zone no longer exists as brittle sheets, needles or nets, it is uniformly distributed in minute globules which give a maximum durability of wearing surface with a total lack of the former extreme brittleness. The core is very fine grained and the martensite instead of occurring in a comparatively few large crystals which would tend to promote brittleness now occur as fine crystals embedded uniformly in a matrix of soft iron.

This brief description of the development of the treatment of a gear is a fair example of the work which has been carried out in the heat treatment of other parts by many automobile plants during the past six or eight years. In a single high grade machine, with the use of seven basic steels, parts are made and treated in different ways, giving 76 different physical properties, designed to withstand to a maximum the various stresses to which each individual part is subjected.

The Christiania Morgenbladet of December 15, 1914, states that the Electric Furnace Products Co. (Ltd.), of Saude, Norway, has applied for incorporation, having already secured the lands necessary and permission to rent up to 84,000 horsepower from A/S Saudefaldene, Saude Falls, the latter company being subsidiary to the Union Carbide Co. (American), which operates and is well known in the United States. The article further states that the American company furnished the capital for the construction of the power plant of A/S Saudefaldene; that 40,000 horsepower are to be delivered to Electric Furnace Products Co. (Ltd.) during four years beginning 1916, to be used in the production of carbide and other electric metallurgical products, the total production of carbide, estimated at 60,000 to 80,000 tons annually, to be exported to the United States. This plant will operate at Saude, Norway, about 50 miles north of Stavanger.



THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Wine Analysis.

Any fermented fruit juice will produce a wine. Cleanliness, temperature and the yeast having the upper hand in the fermentation all have their influence on the final product.

Lack of cleanliness fosters vegetable fungus growths that create undesirable fermentations and spoil the wine.

Temperature influences the final product in that at 25° to 30° C. a rapid fermentation is produced while at 10 to 15° C. a slower one is produced. The rate of fermentation affects the bouquet which is due to the ethers. The higher temperature will give less bouquet or aroma than the lower.

The races of yeast, having the upper hand in the fermentation differ from one another in the products of their fermentation. A wine must, fermented by Jörgensen with different yeasts varied, from two to fourteen per cent of the total alcohol produced, in the glycerine content. The fact that races of yeast differ so in the yield of their fermented products has lead European governments as well as the United States to make extensive experiments with races of yeast to discover those that will give the most desirable qualities. These yeasts are kept and furnished to applicants by bureaus established for that purpose.

Wines are either natural or fortified. The natural wines are those to which no sugar or alcohol has been added, but have been allowed to ferment to the exhaustion of the sugar or yeast nutriment or have been checked by the strength of the alcohol developed. Fourteen per cent strength of alcohol by weight is about the limit to which a yeast can ferment in a wine must. Hock, claret and many California wines are natural. Fortified wines are those to which sugar has been added, as is often done when a poor year has lowered the sugar content of the grapes. The amount added is generally controlled by law in this country as well as in Europe. Alcohol too is very often added. The spirit is generally added before fermentation is completed. The strength is then raised and fermentation is checked. The wine, thereby, is often made sweet due to the unfermented sugars. Madeira, sherry and port are examples of fortified wines.

Wines are also classified by color, taste, and by their positive or negative effervescence. We have the red or white wines, dry or sweet, and still or sparkling.

TABLE I.

	Number of Analyses.	Specific Gravity.	Alcohol by Weight.	Extract.	Total Acid as Tartaric.	Free Tartaric Acid.	Cream of Tartar.	Volatile Acid as Acetic.	Sugar.	Glycerine.	Nitrogen.	Ash.	P_2O_5.	Potash.	Lime.	Magnesia.	Sulphuric Acid.
Germany—																	
Moselle	14	0.9964	7.99	2.24	0.79	....	....	....	0.031	0.72	....	0.175	0.036	0.068	0.011	0.02	0.012
Rhine	23	1.0005	8.00	2.60	0.81	....	0.20	....	....	0.85	....	0.23	0.046	0.085	0.017	0.022	0.020
Baden	46	......	6.65	2.16	0.91	0.018	0.358	....	0.095	0.49	....	0.207	0.025	....	....	....	....
Wurtemburg white wine..	15	0.9995	6.10	2.27	0.95	0.095	0.262	....	....	0.57	....	0.25	0.043	0.115	....	....	0.009
Wurtemburg red wine.....	6	......	4.73	2.64	1.14	0.091	0.026	....	....	0.40	....	0.25	0.040	0.108	0.024	0.010	0.08
Alsace	15	......	6.59	2.07	0.696	0.018	0.168	0.052	....	0.55	0.028	0.229	0.038	....	....	....	....
Lorraine, red wine	10	0.9967	8.08	2.27	0.56	0.032	....	0.155	0.088	0.50	0.019	0.185	0.030	....	....	....	0.008
France—																	
Red wine	29	0.9982	7.80	2.56	0.57	....	....	....	0.30	0.73	0.043	0.248	0.030	0.106	0.101	0.018	0.033
White wine....	5	0.9963	8.30	3.03	0.66	....	....	....	....	0.97	....	0.25	0.032	0.098	0.010	0.015	0.038
Austria—																	
Tyrol red wine	60	0.9940	9.08	2.34	0.62	....	....	....	....	0.65	0.021	0.222,	0.027	....	....	....	0.023
Tyrol white wine	17	0.9927	8.84	1.87	0.59	....	....	....	....	0.65	0.020	0.175	0.022	0.077	....	. . .	0.023
Russia—																	
Red wine	10	0.9939	10.76	2.76	0.56	....	....	0.142	....	0.64	0.036	0.267	0.027	0.111	....	....	....
White wine ...	12	0.9931	11.96	2.568	0.49	....	....	0.100	0.458	0.59	0.026	0.204	0.030	0.086	....	....	....
Italy	20	......	10.61	3.44	0.52	....	....	....	1.44	0.45	....	0.29	0.032	0.115	0.009	0.017	0.019
Spain—																	
Ordinary red wine	7	......	12.30	3.53	0.49	....	....	....	0.38	1.09	....	0.61	0.027	0.242	0.008	....	0.221
Sweet wine ...	4	1.0233	12.78	9.69	0.59	....	....	....	6.55	0.63	....	0.74	0.039	0.296	....	....	0.212

Burgundy, clarets, and Bordeaux wines are red, while the Rhenish, Moselle and Sauternes are white. The skins of the grapes give the coloring matter and are fermented with the pulp before pressing. White wine is made from the pressed pulp freed from the skines at once, or is made from white grapes.

Dry wines are those in which all the sugar has become exhausted by fermentation while sweet wines contain various amounts of unfermented sugar. Madeira, red or white, is a dry wine, while port is an example of a sweet wine. Still wines are those from which carbon dioxide has been exhausted so there is no effervescence. Sparkling wines effervesce due to carbon dioxide and are either heavily charged artificially or the gas is formed by the addition of sugar to the bottles before corking.

In the making of grape wine the quality depends on the care exercised in grading the grapes and careful regulation of fermentation. The grapes are crushed by machinery, and in some localities by the bare feet. The juice is then pressed from the pulp by machinery.

König's analyses of a large number of grape musts is here summarized below:

	Specific Gravity.	Water Per Cent.	Nitrogenous Material.	Sugar.	Acid.	Other non-nitrogenous material.	Ash.
Minimum	1.0690	51.53	0.11	12.89	0.20	1.68	0.20
Maximum	1.2075	82.10	0.57	35.45	1.18	11.62	0.63
Mean	1.1024	74.49	0.28	19.71	0.64	4.48	0.40

The must is fermented either by the addition of a special type of yeast or by the yeast occurring by accident on the grapes. According to the type of yeast doing the fermenting, rate of fermentation, and temperature various amounts of the following are produced: Ethyl alcohol, glycerine acetic acid, aldehydes, volatile ethers, fixed ethers, succinic acid and probably traces of the higher-boiling alcohols—propyl, butyl and amyl. These products of fermentation, the organic acids in the fruit, the mineral salts, coloring matter from the skins, and a large bulk of water form the wine.

Typical analyses due to König, of German, French, Austrian, Russian, Italian and Spanish wines are given in Table I.

The following standards have been adopted by the United States: "Wine is the product made by the normal alcoholic fermentation of the juice of sound, ripe grapes and usual cellar treatment, and contains not less than 7 nor more than 16 per cent alcohol by volume, and in 100 c. c. (20° C.) not more than 0.1 gram of sodium chloride nor more than 0.2 grams of potassium sulphate; and for red wine not more than 0.14 gram and for white wine not more than 0.12 gram of volatile acids produced by fermentation and calculated as acetic acid. Red wine is wine containing the red coloring matter of the skins of grapes. White wine is made from white grapes or the expressed fresh juice of other grapes.

"Dry wine is wine in which the fermentation of the sugars is practically complete, and which contains, in 100 c. c. (20° C.) less than 1 gram of sugars, and for dry red wine not less than 0.16 gram of grape ash and not less than 1.6 grams of sugar-free grape solids, and for dry white wine not less than 0.13 gram of grape ash, and not less than 1.4 grams of sugar-free grape solids.

"Fortified dry wine is dry wine to which brandy has been added but which conforms in all other particulars to the standard of dry wine.

"Sweet wine is wine in which the alcoholic fermentation has been arrested and which contains in 100 c. c. (20° C.) not less than 1 gram of sugars, and for sweet red wine not less than 0.13 gram of grape ash."

Fortified sweet wine is sweet wine to which wine spirits have been added. By Act of Congress "sweet wine" used for making fortified sweet wine and "wine spirits" used for such fortification are defined as follows: "Wine spirits is the product resulting from the distillation of fermented grape juice to which water may have been added prior to, during, or after fermentation for the sole purpose of facilitating the fermentation and economical distillation thereof, and shall be held to include the products from grapes or their residues, commonly known as grape brandy; and the pure sweet wine, which may be fortified free of tax, as provided in said section, is fermented grape juice only, and shall contain no other substance whatever introduced before, at the time of, or after fermentation except as herein expressly provided; and such sweet wine shall contain not less than 4 per cent of saccharine matter, which saccharine strength may be determined by testing with Balling's Saccharometer or must scale, and such sweet wine, after the evaporation of the spirits contained therein, and restoring the sample tested to original volume by addition of water: Provided, that the addition of pure boiled or condensed grape must, or pure crystallized cane or beet sugar, or pure anhydrous sugar, to the grape juice aforesaid or the fermentation product of such grape juice prior to the fortification provided by this act, for the sole purpose of perfecting sweet wine according to commercial standard, or the addition of water in such quantities as may be necessary in the mechanical operation of grape conveyors, crushers, and pipes leading to fermenting tanks, shall not be included by the definition of pure sweet wine aforesaid: Provided, however, that the cane or beet sugar, or pure anhydrous sugar or water so used, shall not, in either case, be in excess of 10 per cent of the weight of the wine to be fortified under the act: And, Provided, further, that the addition of water herein authorized shall be under such regulations and limitations as the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury may from time to time prescribe; but in no case shall such wines to which water has been added be eligible for fortification under the provisions of this act where the same, after fermentation and before fortification, have an alcoholic strength of less than 5 per cent of their volume.

"Sparkling wine is wine in which the after part of the fermentation is completed in the bottle, the sediment being disgorged and its place supplied by wine or sugar liquor, and which contains in 100 c. c. (20° C.) not less than 0.12 gram of grape ash.

"Modified wine, ameliorated wine, corrected wine, is the product made by the alcoholic fermentation with the usual cellar treatment of a mixture of the juice of sound ripe grapes, with sugar (sucrose) or a syrup containing not less than 65 per cent of sugar (sucrose) and in quantity not more than enough to raise the alcoholic strength after fermentation to 11 per cent by volume.

"Raisin wine is the product made by the alcoholic fermentation of an infusion of dried or evaporated grapes, or of a mixture of such infusion, or of raisins with grape juice."

Table II is a list of American wines analyzed by Bigelow.

Grape wine is adulterated in many ways: by watering, by addition of alcohol, by addition of excessive amounts of sugar or glucose, by coal tar and vegetable colors, by antiseptics, by flavoring compounds, by using apple stock as the basis, and by "Plastering."

Watering of wine, unless excessively done, is very difficult to detect due to the varying composition of the grapes. Large amounts, of course, would abnormally lower the alcohol, extract, ash, acidity and nearly all the constants. Gautier in his "Traité sur la Sophistication et l'Analyse des Vins" claims that the sum of the weight in grams of alcohol in 100 c. c. and the total acidity, expressed in grams of sulphuric acid per liter, varies rarely below 13 or above 17. Added water therefore, would be indicated if the sum of the constants was reduced below 13.

A relation existing between the weight of the extract and that of alcohol was submitted in France by a committee whose duty it was to report on the addition of alcohol to wine. If the weight of the alcohol divided by the weight of the extract (both expressed in grams per 100 c. c.) exceeds 4.6 for red wines, the addition of alcohol may be strongly suspected, while in the case of white wines this quotient should not exceed 6.6.

It is frequently important to know the nature and the amount of sugar present in wine. This information is arrived at by making the direct and invert polarization of the wine, and by running a determination for reducing sugars.

The polarization of pure wine is nearly always left-handed unless, of course, all the sugar is fermented, and then the reading will be zero. This is due to the dextrose being more fermentable than the levulose. If

TABLE II.

				Grams per 100 cc.			Grams per 100 cc.			—— Grams per 100 cc. ——				
	Number of Samples.	Specific Gravity.	Per cent Alcohol by Volume.	Alcohol.	Glycerine.	Glycerine-Alcohol Ratio.	Total Acids.	Extract.	Polarization.	Reducing Sugar.	Potassium Sulphate.	Proteids.	Tannin and Coloring Matter.	Ash.
Red Wines—														
Bordeaux or Claret type—	81													
Maximum		1.0020	15.09	11.97	0.852	8.7:100	0.888	3.81	—2.1	0.628	0.1570	0.5544	0.358	0.429
Minimum		0.9900	8.92	7.09	0.330	3.4:100	0.368	2.09	—0.5	0.040	0.0470	0.1865	0.064	0.209
Rhine type—	6													
Maximum		0.9970	13.82	10.96	....	......	0.718	3.31	....	....	.....	.....	0.349	....
Minimum		0.9940	11.00	8.73	....	......	0.358	2.69	....	....	.....	.....	0.211	....
Red Burgundy type—	25													
Maximum		0.9962	15.48	12.29	0.956	7:100	0.762	3.46	—1.7	0.418	0.2515	0.4482	0.328	0.416
Minimum		0.9911	8.00	6.35	0.461	4.7:100	0.408	2.10	—0.5	0.030	0.0455	0.1864	0.033	0.188
Southern French type—	92													
Maximum		1.0050	19.28	15.30	....	......	0.834	6.88	....	....	.....	.....	0.344	0.430
Minimum		0.9900	8.07	6.40	....	......	0.201	1.91	....	....	.....	.....	0.050	0.202
White Wines—														
Rhine Wine type—	87													
Maximum		1.0020	14.57	11.57	0.971	10.2:100	0.788	4.38	—3.5	0.626	0.1771	0.5164	....	0.447
Minimum		0.9883	5.00	3.98	0.474	4.6:100	0.327	1.51	—0.2	0.060	0.0633	0.0989	....	0.140
Sauterne type—	55													
Maximum		1.0157	15.20	12.07	0.904	7.7:100	0.766	6.78	+0.6	3.569	0.1648	0.3809	0.087	0.368
Minimum		0.9892	8.23	6.53	0.178	1.8:100	0.377	1.69	—18.6	0.069	0.0453	0.0867	0.015	0.050
Southern French type—	63													
Maximum		0.9988	22.18	17.60	0.918	1.4:100	0.656	4.56	—3.4	0.936	.....	0.3162	0.045	0.290
Minimum		0.9882	8.07	6.40	0.318	3.4:100	0.219	1.09	—0.1	0.069	.....	0.0988	0.034	0.148
Port type—	50													
Maximum		1.0429	22.19	17.61	0.707	4.5:100	0.700	17.22	—27.1	13.559	0.1861	0.9379	1.066	0.394
Minimum		0.9875	10.38	8.24	0.163	1.1:100	0.181	2.43	—14.4	0.228	0.0594	0.1893	0.059	0.222
Sherry and Madeira type—	66													
Maximum		1.0560	21.85	17.34	0.936	6.8:100	0.798	19.66	—23.1	17.210	0.1196	0.4751	0.350	0.436
Minimum		0.9866	8.22	6.52	0.324	2:100	0.253	1.31	—0.5	0.119	0.0504	0.0859	0.021	0.156

commercial glucose or cane sugar has been added to a wine a sharp right-handed polarization is found. If, after inversion, right-handed polarization is still found, this indicates glucose. If the inversion changes the right-handed reading to left, cane sugar has been added.

Many colors are used to color wine. The principal ones are fuchsin, acid fuchsin, and cochineal.

The antiseptics are used as preservatives. Boric and salycilic acid are normal in some wines and their detection should be quantitative. Sulphurous acid should also be quantitative.

Flavoring principles, as elderberry flowers, bitter almonds, etc., are used very often in composition wines to duplicate various well known brands.

Apple stock is very often used as the basis to make wine. This is then flavored, colored, and by addition of sugar allowed to ferment. This spurious grape wine may be detected by a flame test. The potash flame is readily seen when apple stock has been used, while in a pure grape wine the sodium flame predominates.

By "plastering" is meant the addition of calcium sulphate (plaster of Paris) to the must before fermentation. This practice is in vogue in France, Italy and Spain. The $CaSO_4$ reacts with the potassium bitartrate present in grape wine. It is claimed that this clarifies the wine by carrying down mechanically impurities, increases solubility of the coloring matter, aids fermentation by making it more rapid and complete, and enhances keeping qualities. The effects of plastering increases the ash, and is, in some countries, forbidden.

In judging the purity of a wine the following determinations are most valuable: alcohol, extract, glycerol, ash, total and volatile acids, reducing sugar, coloring matter and preservatives.

The actual percentage of the above is not so important as the relation between them such as alcohol to glycerol, alcohol to acids, and volatile acids to total acids.

1. SPECIFIC GRAVITY.

Determine at 15.6° C. by means of a pyknometer, Westphal balance or a small accurately graduated hydrometer.

2. ALCOHOL.

Place 100 c. c. of the wine at 15.6° C. and 50 c. c. of water in a distillation flask of about 300 c. c. capacity. Attach the flask to a vertical condenser and distill almost 100 c. c. making up to 100 c. c. at 15.6° C. If foaming occurs add a small amount of tannin. If acetic acid fermentation has set in strongly, add 0.1 to 0.2 grams of precipitated calcium carbonate. Determine the specific gravity of the distillate as under 1 and obtain corresponding percentage of alcohol by volume and grame per 100 c. c. from tables in Leach, government bulletins, or some chemical handbook. The weight of the distillate times the per cent of alcohol divided by the weight of the sample equals the per cent of alcohol by weight.

3. EXTRACT.

(a) In Dry Wine.

Evaporate 50 c. c. of the sample on the water bath to a syrupy consistency in a flat-bottomed platinum dish approximately 85 mm. in diameter and of about 75 c. c. capacity. Heat the residue for two and one-half hours in a drying oven at the temperature of boiling water and weigh. The sugar free extract is found by deducting the weight of sugar in excess of 0.1 gram per 100 c. c. from the total residue. In the case of plastered wines, the potassium sulphate in excess of 0.1 gram is also deducted.

(b) In Sweet Wines.

When the extract content is between 3 and 6 grams per 100 c. c. treat 25 c. c. of the sample as described under (a) of dry wines. If the extract exceeds 6 grams per 100 c. c. the approximate determination of the extract is made by consulting tables compiled by Windisch. A measured portion of wine is evaporated on water bath to one-fourth its volume, and then diluted with H_2O exactly to volume measured. The specific gravity of this dealcoholized liquid is determined at 15.6: C. and from Windisch tables the corresponding extract for the specific gravity is read off. This latter method must be used due to the serious error involved with drying levulose at high temperature. Windisch tables are in Leach, Bulletin 107, and books on wine analysis.

4. GLYCEROL.

(a) In Dry Wines.

One hundred c. c. of the wine are evaporated on the water bath to a volume of about 10 c. c. 1 or 2 grams of fine sand are added and sufficient milk of lime added to make alkaline. Continue evaporation nearly to dryness, cool, and shake with 50 c. c. of 95 per cent alcohol; heat to boiling on the water bath, and filter. The insoluble residue is washed on the filter paper, with several portions of hot alcohol, using about 100 c. c. and the washings added to the original filtrate. The alcoholic filtrate is evaporated to a sirupy consistency on the water bath. This residue is then dissolved in 10 c. c. of absolute alcohol and transferred to a flask with 15 c. c. of ether. The flask is tightly corked, shaken and allowed to stand for some time. Filter into a tared dish, wash with a mixture of absolute alcohol (1 part) and ether (1.5 parts); evaporate the filtrate to a sirupy consistency on the water bath, dry in a water oven foi one hour and weigh as glycerine.

With plastered wines the results are too high because of the potassium sulphate that is present and decomposed by the lime to form potassium hydroxide, which is soluble in glycerine and alcohol. In plastered wines the above residue should be ignited and the ash deducted from the above weight.

(b) Sweet Wines.

In the case of sweet wines, (containing more than 5 per cent of sugar) only 50 c. c. of the wine are used for the estimation of the glycerine. The sand and lime are added and the mixture warmed on the water bath. After cooling treat with 100 c. c. of 95 per cent alcohol, allow the precipitate formed to settle, filter, and wash the insoluble matter with spirit. The alcoholic filtrate obtained is then treated as above described.

GLYCEROL-ALCOHOL RATIO.

Express this ratio—X:100, in which X is obtained by multiplying the per cent by weight of glycerol by 100 and dividing the result by the percentage by weight of alcohol.

5. DETERMINATION OF POTASSIUM SULPHATE.

100 c.c. of the sample is acidified with hydrochloric acid heated to boiling and an excess of barium chloride solution added. Filter, wash, dry, ignite and weigh as barium sulphate. Calculate the equivalent of potassium sulphate. If more than .06 grams per 100 c.c. is present, plastering is indicated.

6. ASH.

Weigh two grams of the extract dried and burn until free from carbon at the lowest possible heat.

7. ASH-EXTRACT RATIO.

Express results as 1:X in which X is the quotient obtained by dividing the percentage of extract by the percentage of ash.

8. TOTAL ACIDITY.

In carbonated liquors the carbon dioxide is first expelled by pouring the wine back and forth from one beaker to another and from time to time removing the excess froth on top of the vessel by aid of the hand. 25 c.c. of the sample is taken and heated just to the boiling point and then titrated with tenth-normal sodium hydroxide, using in the case of white wine phenolphthalein as an indicator. With red wine delicate litmus paper should be used. Total acidity is calculated as tartaric acid. Each c.c. N/10 alkali corresponds to .0075 grams tartaric acid.

9. VOLATILE ACIDS.

The volatile acid is expressed as acetic. 50 c.c. of the wine and a little tannic acid are transferred to a distilling flask the stopper of which is provided with two tubes. One leads to a flask containing about 300 c.c. water and the other tube connects to a distilling flask. Contents of both flasks are brought to boiling. The flame of distilling flask is lowered and a flow of steam is sent through the distilling flask from the water flask until about 200 c.c. of distillate is collected in a receiving flask. This distillate is titrated with N/10 NaOH, phenolphthalein as indicator. Each c.c. of N/10 NaOH is equivalent to 0.006 gram acetic acid.

10. FIXED ACIDS.

Determine by difference of the total acidity and volatile acids. The volatile acids being calculated for purpose of subtraction in terms of tartaric acid or other acid that total acidity is expressed in.

11. DETECTION OF FREE TARTARIC ACID—NESSLER'S METHOD.

A small portion of wine is shaken at intervals in a corked flask with some powdered cream of tartar. The liquid is then filtered and to the filtrate a little 20 per cent potassium acetate solution is added. The liquid is stirred and if any free tartaric acid is present there will be a precipitate of cream of tartar. If no precipitate let stand a while and examine again.

12. TOTAL TARTARIC ACID.

2 c.c. of glacial acetic, 15 grams of powdered potassium chloride, and 3 drops of a 20 per cent solution of potassium acetate are added to 100 c.c. of wine. This mixture is then stirred to hasten the solution. 15 c.c. of 95 per cent alcohol is added and the side of beaker is rubbed vigorously with a glass rod to start crystallization. Allow to stand 15 hours at room temperature. Decant through a gooch with a thin film of asbestos. Do this rapidly and allow no more of the acid potassium tartrate to be transferred on the gooch than possible. The precipitate is then washed three times with a small amount of a mixture of 15 grams potassium chloride, 20 c.c. of 95 per cent alcohol, and 100 c.c. of H_2O using no more than 20 c.c. of the wash solution in all. Transfer the asbestos film and precipitate to the beaker in which the precipitation took place, wash out the gooch with hot water, and add 50 c.c. of hot water, heat to boiling and titrate the hot solution with decinormal sodium hydroxide, using delicate litmus tincture or litmus paper as indicator. Increase the number of cubic centimeters of decinormal alkali employed by 1.5 on account of the solubility of the precipitate. This figure multiplied by 0.015 gives the amount of total tartaric acid in grams per 100 c.c.

13. CREAM OF TARTAR.

Ignite the residue obtained from the evaporation of 50 c.c. of wine as directed under ash determination. Exhaust the ash with hot water, add to the filtrate 25 c.c. of decinormal hydrochloric acid, heat to incipient boiling, and titrate with decinormal alkali solution using litmus for an indicator. Deduct from 25 c.c. the number of c.c. of N/10 alkali employed and multiply the remainder by 0.0188 for potassium bitartrate expressed in grame.

14. FREE TARTARIC ACID.

Ash 50 c.c. of wine. Add 25 c.c. of N/10 HCl, heat to incipient boiling and titrate with N/10 NaOH using litmus as indicator. Deduct the number of c.c. employed from 25 and multiply the remainder by 0.0075 to obtain the amount of tartaric acid necessary to combine with all the ash (considering it to consist entirely of potash). Deduct the figure so obtained from the total tartaric acid for the free tartaric acid.

16. REDUCING SUGAR.

Determine as dextrose by Defreu or the Allihn method. For this purpose dilute a measured portion of the wine and evaporate on the water bath to one-fourth its original volume. Clarify with sub-acetate of lead and add enough water so that solution contains one-half of one per cent of sugar for the Defreu and about 1 per cent of sugar for the Allihn method. One may assume 2 per cent as the sugar free extract of wine, the number of volumes of water to be added to the filtrate being determined by the difference between 2 and the total extract as determined.

17. TANNIN.

A method by Nessler and Barth is an approximate one for determining tannin. To 12 c.c. of wine add 30 c.c. of alcohol and filter. Evaporate 35 c.c. of the filter, which corresponds to 10 c.c. of wine, to about 6 c.c. and transfer to a 10 c.c. graduated centrifuge tube. Add a few drops of 40 per cent sodium acetate and a slight excess of 10 per cent ferric chloride. The tube is corked, gently agitated and allowed to stand 24 hours. Then measure the volume of precipitate. Each c.c. of precipitate is equivalent to .033 per cent of tannin in the wine.

18. FOREIGN COLORS IN WINE.

Colors most commonly found in wine, are cochineal, fuchsin and acid fuchsin.

The Pharmacopeia gives the following color tests:

If 2 c.c. of red wine are mixed in a test tube with 2 drops of chloroform and 4 c.c. of normal potassium hydroxide and the mixture carefully heated, the disagreeable odor of insonitril should not become perceptible (absence of various aniline colors).

If 50 c.c. of red wine be treated with a slight excess of ammonia water the liquid should acquire a green or brownish-green color; if it be then well shaken with 25 c.c. of ether, the greater portion of the ethereal layer removed and evaporated in a porcelain capsule with an excess of acetic acid and a few fibres of uncolored silk, the latter should not acquire a crimson or violet color (absence of fuchsin).

If 25 c.c. of red wine heated to about 45° C. be well agitated with 25 grams of manganese dioxide, the liquid filtered off and acidulated with hydrochloric acid, it should not acquire a red color (absence of sulphofuchsin).

DUPRES METHOD OF DETECTION.

Small cubes of jelly measuring about 2 cm. in thickness are prepared as follows: Dissolve 1 part pure gelatine in 10 parts boiling water and pour upon a plate to harden. This is then cut into cubes as mentioned above. A suspected wine is treated by immersing one of these cubes therein for 24 hours after which it is removed and washed slightly in cold water and cut through with a knife. If the color is a natural one it will lightly tinge the outer surface of the cube, but will not permeate far below the surface, so that the inner portion of the cross section will be largely free from color. Nearly all foreign coloring matter used in wine such as most coal-tar dyes, cochineal, Brazil wood, logwood, etc., will be found to deeply permeate the jelly cube often to the center. Information as to the nature of the color may sometimes be gained by immersing the dyed jelly cube in weak ammonia. If the color be rosanilin, the cube is decolorized; if cochineal, a purple coloration will result, and if logwood, a brown tinge.

METHODS OF ANALYZING VEGETABLE PARCHMENT.*

The usual method of disintegrating a sample of paper for examination of the fibrous constituents under the microscope is not readily applicable to vegetable parchment, since the fibers of the latter firmly adhere to one another and cannot easily be separated. For ordinary papers it is sufficient, Sindall and Bacon say, in the *Paper Makers' Monthly Journal,* to warm a fragment of the sample gently in a weak solution of caustic soda which is then washed out thoroughly with hot water. The paper is disintegrated by shaking in a bottle or test tube and is then ready for examination. Such a process fails to disintegrate vegetable parchment, and other processes have to be found by means of which the fibers can be loosened one from the other.

In 1909, Vidal proposed a process by which the external surfaces of the vegetable parchment were partly or completely removed by means of ammoniacal cupric oxide, so that the fibers in the interior of the sheet were thereby loosened and rendered suitable for examination. This method, however, is of doubtful value on account of the part solution of some of the fibrous constituents, and while this would be immaterial in the case of a paper composed entirely of one fibrous constituent, it would be useless in a case where the vegetable parchment itself was a mixture of two fibers. The proportion of each present would probably be altered as a solution of this character would not act equally upon two different fibers.

A method has been proposed by Bartsch, making use of sulphuric acid as the reagent, by means of which the hardparchment is reduced to the condition of pulp. He suggests the use of ordinary sulphuric acid having specific gravity of 1.84, diluted with an equal volume of water. About 100 c.c. of this diluted acid is put into a beaker and warmed to a temperature of 50° C., and small pieces of the paper under investigation are vigorously stirred with a glass rod in the warm solution of acid. The paper soon becomes spongy and gradually falls to pieces. As quickly as possible the mixture is thrown into a large beaker containing water so that the resolvent action of the acid is at once stopped. The mass of pulp is then thoroughly washed and examined under the microscope in the usual way.

The process must be conducted quickly and in the shortest possible time, in order to prevent any serious dissolution of the fibers by the sulphuric acid. As a rule an immersion of 2 to 5 minutes is found sufficient. Should it be noticed that the cellulose appears to have been strongly attacked, when observing under the microscope, a fresh quantity of paper must be treated so as to reduce the time of immersion of acid. With parchment made from rags the fibers fairly resist the action of the acid, but with wood cellulose the resistance to acid is not so great.

Bartsch appears to have made many experiments in this direction and seems to be satisfied with the process, but it is evident that this method has the same disadvantages as that found in the process of Vidal. However carefully the operation is performed, a sensible change in the condition of the fibers must take place, and probably the resultant product consists of greatly disintegrated fiber together with a few fibers which in the case of thick papers have not been acted on by the acid. It is difficult to see how a very thin vegetable parchment, through which there has been a complete penetration by sulphuric acid in the act of parchmentizing, can possibly be disintegrated sufficiently without material change in composition by such a process.

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*From Paper.

We ourselves [Sindall and Bacon] prefer the little extra trouble which is necessary in order to break up the pulp by mechanical methods. For this purpose a small vertical coffee mill answers very well. Half a gramme or less of the paper is crumpled up with hot water, then torn up into small pieces and put through the mill several times with a little water. The friction of the pieces of paper upon themselves and between the surfaces of the mill in close contact with one another reduces the paper to a fibrous condition. The pulp mass consists of fibers which are separated fairly completely, and there is no difficulty in mounting these for examination under the microscope. It is an advantage to employ the zinc chloride iodine solution in somewhat dilute form so that the mass of pulp is only slightly stained, since the solution of ordinary strength if applied to the fibers renders them such a dense blue color as to make them practically opaque.

The determination of the proportion of wood cellulose in a mixture of rag and wood requires that the solution used for staining should be of the right strength, and this can be easily obtained by trial. The wood fibers in a vegetable parchment which has been well parchmentized lose many of the characteristics by which they are generally recognized when examined with the microscope.

The output of sulphur produced in the Hokkaido has been showing an increasing tendency since January, 1914. The exports of sulphur to Australia had a check on the outbreak of war, but the consumers in North America who had heretofore been getting their supplies from Italy were now constrained to buy of Japan, thus causing increased activity in the export trade of this commodity. As a result the working of the sulphur mines in the Hokkaido became more active, the output of the principal mines there amounting to 10,413,729 lbs. during the month of October. The total for the first 10 months of the year amounted to 85,148,235 lbs., or an increase of about 27,000,000 lbs. over the figures for the similar period of 1913.

China clay, valued at $2,012,225, was invoiced for the United States during last year at the American consulate at Plymouth, England, compared with $1,813,703 worth for 1913.

FLOURISHING MINING INDUSTRY IN PHILIPPINES.

Mining men of the Philippines are practically agreed, states a recent Daily Commerce Report, that the period of experimentation in that industry has passed and that a steady increase in the gold output of the islands for an indefinite period may now be confidently expected. The export figures of recent years seem to bear out this conclusion. New centers of operation are constantly being opened up and new machinery put in place.

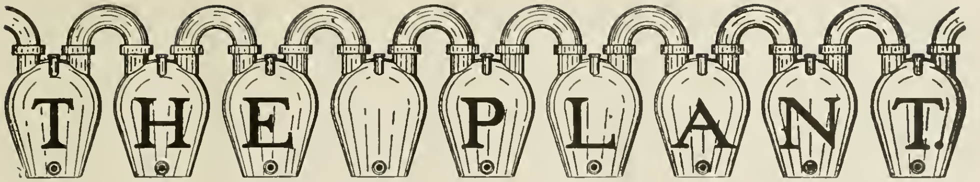
In the mountains of Benguet, where the industry had been suspended for some years owing to lack of funds for development in some instances and to destructive storm damage in others, several mines have resumed operation on a scale which the operators find paying, and development work on a number of other promising projects has started. The recent finds in Mindoro, reported in a former communication, have been followed by other promising locations in that region. An extensive project in Surigao is now being developed and expensive machinery installed in one of the richest fields yet discovered. The mines on the island of Masbate are now producing regular monthly outputs practically up to the capacity of their modern plants, and the same may be said of the Gumaos region.

In the latter field one company reports concerning 149 recent soundings with 4-in. Empire drills that 83 gave no results, being on a hillside not regarded as good dredging ground, while 75 soundings showed results as follows:

Twenty-three tests show an average value of $.019836 per cu. yd., covering a lot of ground containing 160,000 cu. yds.; 23 other tests showed an average value of $0.1671, covering ground containing 210,000 cu. yds.; 23 other tests showed an average value of $0.2694 per cu. yd., covering 194,000 cu. yds. Two other tests showed an average value the one of $2.92 and the other of $2.28. The last two tests mentioned were not taken into account in estimating the averages; had that been done the average for the entire area covered by the 75 soundings would have been $0.495 per cu. yd. The valuable ground sounded covered 564,000 cu. yds., with an average value of $.2111, or a total value of $218,093.

The ground outlined above is expected to keep one dredge working for about eight months, making allowances for the most unfavorable conditions likely to be met in the operation of the dredge. The savings of the dredge on this ground should be $13,200 to $14,100 per month. The ground covered by the report is only a small portion of the holdings of the company, which is but one of many in the Gumaos region.

The gradual expansion of the gold exports, which have now come to be regarded as a permanent part of the commerce of the Philippines, is well illustrated by the figures of the customhouse for the years 1912 and 1913, which show total gold exportations of $77,847 and $729,503, respectively.



THE NEW KNOWLEDGE OF COAL AND ITS PRACTICAL APPLICATION.*

By HORACE C. PORTER.

INTRODUCTION: THE INDUSTRIAL IMPORTANCE OF COAL.

The question may be asked: Why should a chemical engineering course begin with a lecture on coal? Is the efficient use of coal a fundamental thing in engineering?

Unquestionably power production stands as one of the foundation stones in the structure of any industry, and of the total power which operates modern industries at least 80 per cent is derived from the combustion of fuel, a chemical process. Coal, and the coke and gas made from it, constitute 85 per cent of the industrial fuel of America.

Proportionate cost of power varies widely in the different industries, but taking them as a whole, census reports show that fuel constitutes about 8 per cent of the operating costs (exclusive of the cost of materials) in manufacturing industries. The importance of efficiency in the use of fuel becomes at once apparent. Over 150,000,000 tons of coal are used for industrial power. If the percentage utilization of the energy of this coal were everywhere increased by 8 per cent, an increase entirely possible through the use of modern, improved, steam engineering appliances and of the gas producer and gas engine, the cost of the industrial fuel used in the United States would be cut in two, and at least $150,000,000 saved. If all the coke produced in the United States in 1913 had been made in by-product ovens, $80,000,000 worth of by-products might have been saved and $10,000,000 in higher yield of coke.

Coke is by far the biggest mineral product of the United States. The production in 1913 was about 570,000,000 tons and the bulk of this was consumed in our own land. The nation's coal bill was therefore in the neighborhood of 1½ billions of dollars or $60 for each wage-earner per annum. The United States is far ahead of other nations in coal production, having passed Great Britain, the nearest competitor, in 1899, and now surpassing her by nearly 100 per cent. Since we export very little coal and other nations export a great deal, our home consumption surpasses that of other countries by even a much greater margin. Our industries are greater, to be sure, but we must face the fact also that an abundance of fuel resources has made us careless of efficiency in their use.

The coal reserves of this country are immense, the most recent estimates of the United States Geological Survey (for the XII International Congress of Geology, Canada, 1913) showing 1,500 billions of tons easily available, not including the sub-bituminous and lignite coals, these being not now widely used. If production should increase in the future at the rate it has in recent years, the exhaustion of our high-grade reserves may come at no very distant day. But unquestionably there will be a tendency toward a lesser rate of increase in consumption as the present movement toward greater efficiency in the mining and use of coal gains headway and brings results.

We may inquire somewhat analytically: What are the uses of coal and in what ways can they be made more efficient? The 570 millions of tons produced in 1913 in the United States were used approximately as follows:

Domestic	120,000,000
Other heating of buildings	85,000,000
Coke and gas	75,000,000
Locomotives and steamboats	110,000,000
Industrial power (including central power plants)	180,000,000

Scientifically the methods of utilizing coal may be classified into (1) combustion, (2) carbonization, and (3) gasification by partial combustion. Probably 80 per cent of the coal consumption in America comes under class (1), i. e., it is directly burned in air, and we see therefore the great importance of improving practical methods and appliances for combustion.

COMBUSTION.

When we analyze combustion as ordinarily carried out in practice we find all three of the fundamental processes going on. Coal does not burn as a whole on the furnace grate. The upper layers of the fuel bed undergo decomposition by destructive distillation, liberating 15 to 40 per cent of the coal as volatile gases and vapors, while combustion of the residual material is going on in the lower portions of the bed. Gasification of the carbon to CO also constitutes an important part of the burning process, the fuel bed acting as a gas-producer.

Smoke prevention is essentially a problem of proper handling and thorough combustion of the volatile products of the coal; in fact, furnace efficiency is to an important degree dependent on the same factor. The successful and efficient operation of a coal-burning furnace requires an understanding of the nature and behavior of the volatile matter of coal, and especially of that of the particular coal that is used in each case. Something as to the new knowledge of the volatile matter of coal will be presented later, after there have been considered briefly other methods of utilizing coal.

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*Lecture delivered before the Department of Chemical Engineering, University of Pittsburgh, Nov. 9, 1914, by permission of the Director of the U. S. Bureau of Mines. This was the first of a series on recent advances in chemical engineering given as an evening course largely to graduate students.

CARBONIZATION.

Carbonization, from the point of view of fuel efficiency, deserves a much greater industrial application than is now given it. It enters as a factor to be sure, into all the applications of coal, and in coke and gas manufacture it constitutes the essential factor. But only a small percentage of the coal produced goes into coke and gas manufacture.

In carbonization the coal is decomposed under the influence of heat, without access of air, and the entire substance other than the mineral constituents breaks down into volatile products and a fixed residue, principally carbon and ash. The volatile matter of the coal here again comes into play as an exceedingly important phase of the process. The manner of the first breaking down of the coal substance as it begins to be heated probably determines in large measure what quality of coke the coal will form. The early or primary volatile products and the kind of heat treatment they receive as they issue from the retort determine the gas and by-product yields of the coal.

Instead of carbonizing and burning in a single operation as is done in a combustion furnace using coal, whereby all of the coal and the intermediate products evolved from it are burned for their heating value only, the coke oven or gas retort utilizes the coal more scientifically by converting it into two improved forms of fuel, coke and gas, with a combined heating value about 85 per cent of that of the coal, and in addition thereto saving the intermediate by-products tar, benzol and ammonia, which have a chemical value far exceeding their fuel value. The coke and gas as fuels can be burned without smoke and with greater efficiency than the raw coal. A portion of the coke or of the gas, to be sure, must be used to supply the heat for carbonizing, this item amounting usually to from 10 to 14 per cent of the original heat units in the coal.

It is not an idle dream to look forward to the time when there will be many central power and heating stations in the form of large by-product coke-oven plants, placed at the mines or near large cities. As influences leading to this end, we may mention the following: Modern advances in long-distance transmission of electric power, the increasing demand for and value of coal by-products for chemical purposes, the successful use of coke as a domestic and industrial fuel, the development of the gas engine, and the growth of public opposition to the smoke nuisance.

Low-temperature or medium-temperature carbonization of coal has lately been introduced in Europe on an industrial scale. Coal is heated at 500° to 700° C. either under reduced pressure or in a current of auxiliary gas which passes directly through the coal, producing high yields of tars or oils and a rich gas in small quantity. These processes depend for their commercial success on the quality of and the demand for the oils and the solid residues produced. Because of their adaptability to the recovery of oils, possibly motor fuels, from coals not heretofore commonly used for by-products, they offer an interesting field for industrial experiment in the United States. In the present commercial situation brought on by the European war the lack of an adequate supply of creosote oil, largely a coal-tar product, is a big incentive to the increase of coal-carbonizing operations in this country. Sufficient coal tar and benzol can be produced from existing by-product coke ovens and gas retorts to supply the present American demand for all other coal-tar products, creosote oil being excepted. But in view of the increasing use of benzol for many purposes and of the growing demand for coal-tar products of all kinds, there is an opportunity for a large expansion of the coal-carbonizing industry, in the near future.

GASIFICATION.

As to the third general method or process by which coal is used industrially, namely, gasification by partial combustion, the process is exemplified in the gas-producer, comparatively a very efficient method of recovering the potential energy of the fuel. Carbonization enters into this process also, since at the top of the fuel bed the coal is destructively distilled before passing down to be gasified by the air and steam from below. The gas producer will be treated thoroughly in one of the succeeding lectures of this series.

Having considered the industrial uses of coal in a general way, we may, to advantage, take up now some of the scientific aspects of the problems and allude to some of the more recent findings in this field.

NATURE OF COAL.

It is of interest to inquire first: What is coal? What is its chemical nature and constitution? A knowledge of this would surely be of great value in promoting an understanding of its behavior; in determining, for example, the explanation of the coking property, the cause of spontaneous combustion, or the difference between coals in liability to dust explosions in mines. Unfortunately, however, the problem has proven a most difficult one, and as a result of the work of many investigators during the last 20 years or more, little of a definite nature has been determined. We may say without hesitation that coal is a mixture of complex organic substances which are degradation products of cellulose, resins and gums, and vegetable fats and waxes. Free carbon has never been proven to exist in coal and hydrocarbons are probably not present in an amount greater than 1 per cent.

The problem of the constitution of coal has been attacked chiefly by two methods: (1) Extraction with solvents, and (2) destructive distillation at low temperatures. Extraction, while it has resulted, by use of pyridene, in dissolving and removing 15 to 18 per cent of the coal substance, has not separated any single definite identifiable compound in more than mere traces.

Destructive distillation also has led to no exact results, but it has given, on the other hand, certain well-defined indications of the nature of the substances present. These indications are mainly that coal is made up of a great many complex substances, which have resulted from degradation or decay of plant cellulose, lignose, resins and waxes. These substances in coal are closely graded into one another in chemical nature and composition, except that the cellulose and lignose group is probably more or less sharply distinguished from the resinous group. Within each group are substances in many different stages of alteration by aging. Chemically the cellulosic bodies are distinguished by their higher content of oxygen, by their tendency to combine with or absorb oxygen, and by their thermal decomposition into CO_2 and Co, water of constitution, and paraffin hydrocarbons. The resinous constituents, on the other hand, have a higher content of hydrogen, and less of oxygen, and decompose by heat into hydrocarbons and hydrogen with small quantities of CO_2 and water. The resinous bodies are contained most abundantly in the coking and mature coals of the Appalachian region.

THE VOLATILE MATTER OF COAL.

The term "Volatile matter of coal" is more or less of a misnomer, but serves as well as any other. There is probably little or no material in coal which is volatile without decomposition. What we call "volatile matter" is a mixture of vapors and gases resulting from decomposition of the coal substance by heat. Its composition depends on the kind of coal and also very much on the temperature to which the coal is heated and to which the primary products are subjected. By "primary products" are meant those which form first as the coal slowly rises in temperature. These are in order of their formation, water, hydrogen sulphide, CO_2, various saturated and unsaturated paraffin hydrocarbons and hydrogen. Many, in fact most, of the commonly known constituents of coal gas, coal tar and gas-liquor, such as benzene, naphthalene, pitch and ammonia, are the products of second decomposition of those primary products.

The volatile products of coal we see are not all combustible. From some bituminous coals, completely dried, we obtain by decomposition as much as 10 per cent of noncombustible volatile matter, and from some lower-grade coals even as much as 15 or 18 per cent. So there can be no question that the term "volatile combustible matter" as frequently used is decidedly a misnomer, since from one-eighth to one-half of the volatile matter of coal is non-combustible. It is important to bear this in mind when comparing coals, since those coals having rich, smoky, volatile matter are more difficult to burn efficiently than others having a volatile matter possibly greater in amount but with a larger proportion of inert matter in it.

An organic substance, of the nature of cellulose, produces water and CO_2 (with CO also) on decomposition by heat. When cellulose itself decomposes at temperatures below 500° C., 43 per cent of its weight appears as water and CO_2 in the volatilized products. So also coal produces these things by decomposition, and the more abundantly the less matured and metamorphosed is the coal. We must expect to find an aqueous liquor distilled from coal during its decomposition, and in fact at gas works and coke ovens such is the case, a much greater volume of aqueous ammonia liquor being obtained, especially in the hydraulic mains (the first condensing point) than corresponds to the volume of the waste wash water added.

These facts enable us to draw inferences, at least, as to the chemical character of some of the substances in coal. The younger coals like the lignites and subbituminous coals, must contain large proportions of bodies with —OH and —CHO groupings, like the celluloses, since they produce water and CO_2 so readily; in the more mature coals, like the coking and high-grade steaming coals, there are not as many of these oxygen-bearing groups, but, probably, more of certain highly complex long-chain or many-ringed bodies having side-groups of readily separable hydrogen atoms or alkyls corresponding to the paraffin and possibly the aromatic hydrocarbons. These hydrocarbon groups are set free by heat, and then easily undergo further decomposition into the simple, commonly known products like methane and hydrogen.

The theory of Wheeler (of the British Coal-Dust Experiment Station) and others, that coal contains considerable quantities of certain substances which decompose only about 700° C. and yield principally thus hydrogen and the oxides of carbon, is hardly justified by the experimental date at hand. More reasonably is it to be supposed that the large amount of hydrogen which is produced above 700° C. comes from secondary breaking down of the hydrocarbons first liberated, and of the partially carbonized solid materials left behind, these things not having been present, either of them, as such in the original coal. It is likely that all the organic substance in coal decomposes easily by heat, below 500° C.

The nature of the substances liberated or volatilized from coal by moderate heat throws some light on the coking properties of the coal. If by prolonged heating at 400° C. the coal shows little or no tendency to soften or sinter together, and liberates water and gas but only a small quantity of heavy, viscid tar or pitch, it has not good coking properties. Laboratory tests to show coking quality of coals have never been satisfactory. Several are used which give more or less indication but are not definite. Among these may be mentioned (1) heating to a red heat a small sample enclosed in a covered, well-filled platinum box, and examining the coke bar produced; (2) rubbing or grinding the coal in a mortar and noting the tendency to cake or adhere to the pestle and mortar; (3) analyzing for C, H and O and comparing ratios of O to H.

In recent laboratory experiments in Germany cellulose has been converted into coal by subjecting it to very great pressure with moderate heating.

Certain studies are now in progress to determine methods of increasing yields of some of the by-products of coal carbonization, e. g., the commercially desirable benzol and light oils, through carbonization at low temperatures and subsequent treatment, under carefully controlled conditions, of the tars thus produced.

RATE OF EVOLUTION OF VOLATILE MATTER.

In the utilization of coal, particularly in burning on furnace grates, the rate at which the volatile matter is set free is frequently of greater importance than the total quantity produced. Coals vary greatly in this respect. The following results obtained in the laboratory on three different coals similarly treated (0.4 gram powdered, air-dry coal heated at 1000° C.), bring out this variation:

	5 Seconds.		80 Seconds.	
	Total V. M. Per Cent.	Combustible V. M. Per Cent.	Total V. M. Per Cent.	Combustible V. M. Per Cent.
New River, W. Va. ...	5.8	4.8	20.0	17.5
Pittsburgh, Pa.	9.0	7.5	34.0	28.1
Sheridan, Wyo.	36.0	12.4	49.0	21.6

It may be seen from these data that while the Pittsburgh coal produces finally more combustible volatile matter than the Wyoming, the latter on the other hand liberates considerably the more in the first few seconds of heating.

The rate at which a given coal liberates volatile matter depends, first, on its chemical character, i. e., its ease of decomposition, and, second, on the rate at which heat is supplied to it. The ratio between the quantity of coal heated and the quantity of heat supplied in unit time determines the rate at which any given coal becomes heated. It is therefore not a question of temperature as much as of quantity of heat and quantity of coal. When each particle of coal has attained a temperature of 900° C. its decomposition into coke and volatile matter is practically complete.

SUMMARY—VOLATILE MATTER.

Three points stand out as of importance in connection with the volatile matter—the constituent of coal which is so vital in all processes of coal utilization:

1. The composition as well as the quantity of volatile matter varies greatly between coals.

2. The first products volatilized in the early stages of a coal's rise in temperature are essentially different from the total product as usually obtained. These first primary products are largely tarry liquids, with some water vapor and heavy complex gases. Heating conditions determine the degree of secondary thermaldecomposition of these products and the composition of the final gas and tar.

3. The rate of evolution of the volatile matter from coal is of practical importance and varies considerably with the kind of coal. For a given coal it is dependent upon the relation between the quantity of coal heated and the quantity of heat supplied—not the temperature.

OXIDATION, IGNITION, SPONTANEOUS COMBUSTION OF COAL.

Next to thermal decomposition or the evolution of volatile matter, perhaps the most fundamental process involved in the practical utilization of coal is that of oxidation or burning of the substance as a whole.

Slow oxidation at ordinary temperatures gives rise to spontaneous combustion and deterioration in storage; rapid oxidation has much to do with the initiation and propagation of coal-dust explosions in mines, and with the relative ease of ignition of fuels in general. The process of igniting a combustible substance is not as simple as it may seem on first thought, and just why some fuels ignite more easily than others requires careful analysis.

At temperatures above that of the first appreciable decomposition of the substance (say 250° to 300° C. in case of coal), the process of combustion is complicated by the distillation of combustible gases and vapors and the alteration of the solid material. The gases and vapors of decomposition are not, however, all combustible and in fact those produced from the most readily ignited materials such as wood are largely non-combustible. A splinter of wood held in a flame quickly ignites, it is true, because the gases of decomposition are quickly heated to their ignition temperatures. But we can also ignite the wood easily in a glass tube at 250° C. by passing a current of oxygen over it. Here the ignition cannot be a matter of distilled gases since the temperature used is much below the ignition points of those gases.

Relative ease of ignition is unquestionably dependent to some extent on ease of oxidation, i. e., the rapidity of the reaction of the substance with oxygen. Recent laboratory studies have shown a wide variation among different coals and other combustible substances in their rate of oxidation, and the variation in this property follows the known variation in ease of ignition, in susceptibility to spontaneous combustion, and in rate of deterioration in storage.

The action of oxygen on coal at ordinary temperatures has been shown by recent investigation to consist not in a burning of the carbon to CO_2 nor probably of a burning of the hydrogen to water, but largely of an addition of oxygen to the coal substance. This action develops heat. English investigators have shown that the calorific effect of this oxidizing action at 40° C. amounts to between 2 and 3 calories per cubic centimeter of oxygen consumed only a little less than that produced per c.c. of oxygen when coal is completely burned (3.0-3.5 calories). The rate of oxidation increases rapidly with rise of temperature. A coal which at 30° C. consumes say 10 c.c. of oxygen per 100 grams in an hour, will multiply this rate so rapidly from the effect of its own production of heat, that the temperature would rise to 180° C. in a little over two days if no heat were lost. This would result speedily in ignition if an adequate oxygen supply were at hand.

Spontaneous combustion in stored coal results from this slow oxidation by the air at ordinary temperatures. It is not, in any important degree, a matter of bacterial action, or fermentation. When conditions as to the size of coal and manner of piling are such that the rate of heat production by oxidation is greater than the rate of heat loss by convection currents and radiation, the temperature rises. One of the most important practical considerations is whether an adequate air supply can penetrate to an inner section of the pile where the heat loss is slow. Fine slack coal does not heat seriously in the interior of a pile, if no lump is present. If, however, the interior of a pile consist largely of fine coal and the outer and lower sections of lump with very little fine, one of the worst possible conditions is maintained, and spontaneous fires commonly result from such a set of conditions.

Deterioration of coal in storage is due to slow oxidation, not to loss of volatile matter. The deterioration in heating value is not as great as has commonly been supposed. With high-grade bituminous and semibituminous coals, careful determination has recently shown that this loss amounts to less than 1 per cent in one year's exposure to the weather, and less than 3 per cent in 5 years. With our middle-western and western coals or lignites the loss is greater but probably does not exceed 4 or 5 per cent in one year in any case. Deterioration in size or physical character may be somewhat more serious, and spontaneous heating even though moderate in degree causes very serious loss. Deterioration of any kind may be quite largely prevented by submergence storage under water.

Much more might be said of the new knowledge of coal, if time permitted; of the different ways in which water is held in the coal substance, of occluded gases, of the fusibility or softening of the mineral constituents at high temperatures, of the forms in which nitrogen and sulphur are combined in the coal and how they behave on heating, etc., etc.

From what has been told, however, it is hoped that some understanding may have been given of the importance of scientific knowledge of coal and its behavior and of the practical bearing of this knowledge on everyday industrial problems.

The U. S. Civil Service Commission, Washington, D. C., has announced the following examinations of interest to chemists:

Assistant chemist in chemical metallurgy, to fill vacancies in this position in Bureau of Standards; salary, $1,200 to $1,620 per annum; examination to be held March 3.

Organic chemist, to fill vacancies in this position in Bureau of Science, Manila, P. I.; salary, $1,600 to $2,250; examination March 2.

Inorganic chemist, to fill vacancies in this position in Bureau of Science, Manila, P. I.; salary, $1,600 to $2,250; examination March 2.

CAMPHOR—NATURAL AND SYNTHETIC.*

By PERCY A. HOUSEMAN, PH. D., F. I. C.

Camphor has acquired a special interest within the last ten or twelve years on account of its synthesis on a commercial scale. It represents a good example of a growing tendency to replace natural products by artificially-prepared substances, which are either identical in properties with the materials occurring in nature, or can be profitably used as substitutes for them. The commercial synthesis of India rubber presents a similar problem which has yet to be solved.

NATURAL CAMPHOR.

Natural camphor has been known and prized for many hundred years. The camphor tree (*Cinnamomum Camphora*) belongs to the laurel family, and is indigenous to China, Japan and Formosa. The substance known as Borneo camphor is closely related to the true camphor. Its chemical name is borneol, and it is obtained from *Dryobalanops aromatica*, which grows chiefly in Borneo and Sumatra. Borneo camphor commands a much higher price than Japanese camphor. It is used by the natives for ritualistic and medicinal purposes. Camphor is also obtained from an evergreen semishrub (*Blumea balsamifera*) which is found in Eastern India and Burma, and which yields the so-called "Ngai camphor." Within recent years, many attempts have been made to cultivate the camphor tree in other countries.[1] These experiments, however, are somewhat hazardous, for though the tree thrives well in almost any subtropical climate, and appears not specially subject to attack by insect enemies, about fifty years must elapse before good yields of camphor are obtainable. Individual trees show great variability in the amount of camphor they yield, a phenomenon the cause of which is not well understood.

The question then naturally arises as to the extent of the camphor forests now existing. Until recent years no attempts were made to plant young trees in place of those cut down, but this wasteful policy has now been checked, especially since the Japanese assumed control of the camphor industry after the Chino-Japanese War of 1894.

Between the years 1900 and 1906 some 3,000,000 trees were planted by the Japanese monopoly, and, with the old trees assuring a sufficient supply of camphor for at least fifty years, there is no immediate prospect of a shortage in the supply of natural camphor. The competition which natural camphor encounters with the synthetic article will be treated of later.

The following table[2] shows the value of the camphor (presumably crude and refined) exported from Japan and Formosa for the year 1911-1912:

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*From American Journal of Pharmacy.

[1] See, e. g., Board of Trade Journal, July, 1907, "Camphor Trees in Federated Malay States." B. J. Eaton, Agric. Bull. Straits Settlements and Federated Malay States, 1909. Colonial Office Report, 1907, No. 527, "Camphor Trees in Ceylon." Battandier, J. Pharm. Chem., 1907, 182, "Camphor Trees in Algeria." Chemist and Druggist, 1907, 109, "Camphor Trees in the United States." "Camphor Industry in Foreign Countries," U. S. Department of Commerce and Labor, 1910

Destination—	1911.	1912.
Hongkong	$ 15,438	$ 10,956
British India	285,500	322,000
Straits Settlements	4,034	4,900
England	327,700	362,000
France	398,000	251,500
Germany	260,000	244,500
United States	358,000	228,500
Canada	6,000	10,400
Australia	47,000	37,850
Other countries	24,000	57,800
Totals	$1,725,672	$1,530,406

The camphor output of Japan during 1911 was larger than at any time since 1902, over 2,640,000 pounds having been produced, of which 860,000 pounds were exported, 1,254,000 pounds taken by local refineries, 460,000 pounds by Japanese celluloid factories, the remainder going to general consumers.[3]

The imports of crude natural camphor from all sources into the United States for the fiscal year ending June 30, 1911, amounted to 3,726,319 lbs., valued at $1,118,586. For 1912 the amount was 2,154,646 lbs., valued at $682,669.[4]

China produces less camphor than Japan and Formosa. In 1912 China exported 165 tons, valued at $130,521, and in 1913, 124 tons, valued at $94,298.[5]

The world's production of camphor for 1913[6] is estimated at about 12,000,000 lbs., of which 4,600,000 lbs. are credited to Formosa, 2,000,000 lbs. to Japan, and 1,300,000 lbs. to China, the remaining 4,000,000 being left for natural camphor produced in other countries, and for synthetic camphor.

EXTRACTION AND REFINING.

The extraction of the crude camphor from the tree is a simple process. The wood is cut into chips and subjected to the action of steam in stills of primitive construction. The number of camphor stoves in Formosa in 1910 is given as 7,834, and the number of camphor workers on the island as nearly 30,000.[7] Formosa supplies about one-half of the total crude camphor produced. Camphor is obtainable from all parts of the tree:[8] leaves, twigs, wood and roots.

The crude camphor is divided into three grades, A, B, and BB, and is refined by steam distillation, sublimation, or crystallization. Refined camphor comes into the market as "flowers," "bells," or "blocks." Camphor oil is obtained as a by-product in the extraction of camphor. The oil is used in perfumery, soaps, etc., and contains many essential oils, as well as some dissolved camphor.

PROPERTIES AND USES.

Camphor is a colorless, crystalline substance melting at 175° C. It is volatile at ordinary temperature, and its characteristic odor is said to be detectable at a dilution of 0.000005 gramme camphor in 1 litre of air. One part of camphor requires about 1,000 parts of cold water for solution. It dissolves in organic solvents with ease.

Japanese camphor has a strongly dextrorotatory action on the plane of polarized light, $\alpha_{(D)} = 44.2°$ in alcoholic solution. The lævorotatory camphor occurs in the oil of *Matricaria parthenum* and is known as Matricaria camphor. It is identical with Japan camphor, except for its opposite rotatory power.

Camphor finds application chiefly in three directions:

1. *In Pharmacy.*—Camphor is used in more than thirty different forms. It is antispasmodic, a stimulant, cardiac and local anodyne, and is used in fevers, dysmenorrhœa, colic, etc. Camphor is also used as a disinfectant.

2. *In Explosives.*—Camphor is said to exercise a preservative action on blasting gelatine, but only a small quantity is used in the manufacture of explosives.

3. *In Celluloid.*—Celluloid was invented in 1869 by Hyatt in America, while Daniel Spill worked at the same time in England. The process of manufacture, expressed in a few words, consists of the incorporation of camphor with nitrocellulose and a suitable solvent such as acetone.

The celluloid industry consumes about three-fourths of the total camphor produced, a fact which will be readily understood when one thinks of the enormous number of articles now made of celluloid.

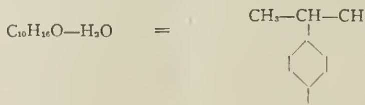
CHEMICAL CONSTITUTION OF CAMPHOR.

This has been a subject of such importance that it is desirable to pass in review the steps leading up to the establishment of the chemical structure of camphor.

Camphor belongs to the important class of compounds called terpenes, the parent substances of this group being unsaturated hydrocarbons possessing the empirical formula C_5H_8. The terpenes fall into four classes: (1) Hemiterpenes (C_5H_8), (2) Terpenes ($C_{10}H_{16}$), (3) Sesquiterpenes ($C_{15}H_{24}$), (4) Polyterpenes $(C_5H_8)_n$.

Camphor is a derivative of the second of the above classes, and possesses the formula $C_{16}H_{16}O$. It is a saturated compound and contains the ketonic group $C - CO - C<-$, forming a well-defined oxime, and yielding a secondary alcohol (borneol) by reduction electrolytically or with sodium amalgam.

When camphor is distilled with phosphorus pentoxie the hydrocarbon cymene (I) is obtained. Cymene is para-methyl-isopropyl-benzene, and the same complex is therefore assumed to be present in camphor.



Camphor (I) Cymene

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[2] Die Chemische Industrie, 36, 355. The figures should be accepted with reserve.

[3] Daily Consular and Trade Reports, No. 229 (15th year), Sept. 28, 1912.

[4] Daily Consular and Trade Reports, No. 261 (15th year), Nov. 5, 1912.

[5] Daily Consular and Trade Reports, No. 262 (17th year), Nov. 7, 1914.

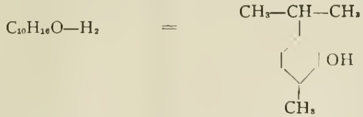
[6] Daily Consular and Trade Reports, No. 75 (16th year), April 1, 1913.

All of the statistics are given as they appear in the original sources of information. In some cases these statistics seem to be contradictory—possibly owing to a lack of clearness in separating figures applying to crude camphor from those applying to the refined article.

[7] "Camphor Industry in Foreign Countries," Special Consular Reports, vol. xliii, part 3, 1910.

[8] See, e. g., B. J. Eaton, Agric. Bull. Straits Settlements and Federated Malay States, 1909. Beille and Lemaire, Bull. Soc. Pharm. Bordeaux, 53, 521. Daily Consular and Trade Reports, No. 255 (16th year), Oct. 31, 1913.

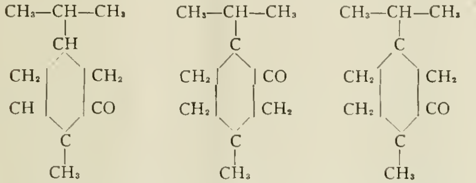
On boiling with iodine, camphor is converted to carvacrol (II), another substance of known structure.



Camphor (II) Carvacrol

The reactions of camphor considered above are satisfied by the formula (III) proposed by Kekulé in 1873. This formula, however, does not account for the saturated character of camphor, nor for its oxidation to camphoronic acid.

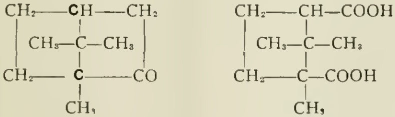
Formula (IV) was put forward by Kannonikow in 1883 and (V) by Bredt in 1884. That Bredt was correct and Kannonikow incorrect in the position assigned to the carbonyl group is proved by the conversion of camphor to carvacrol, considered above.



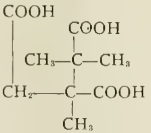
(III) Kekulé, 1873 (IV) Kannonikow, 1883 (V) Bredt, 1884

Bredit later modified his formula to that shown by (VI).

The oxidation of camphor to camphoronic acid is then formulated as follows:



(VI) Camphor (Bredt, 1893) (VII) Camphoric acid

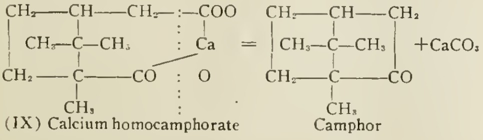


(VIII) Camphoronic acid

Camphoronic acid has been synthesized and is of known constitution (*α-α-β-* trimethyl tricarballylic acid). Lastly, two other points may be mentioned in connection with this complicated question of the structure of camphor.

The first is the partial synthesis of camphor by the distillation of the calcium salt of homocamphoric acid[9] (IX).

This reaction is shown thus—



(IX) Calcium homocamphorate Camphor

The second point is the evidence derived from stereochemical considerations. From Formula (VI) it will be seen that camphor contains two asymmetric carbon atoms (printed in heavy type). To these asymmetric atoms camphor owes its optical activity. If now the carbonyl (CO) group be reduced to (CH_2), the asymmetry of both carbon atoms is destroyed, and the resulting compound must be inactive. This is entirely supported by the experimental results. Bredt's formula for camphor is the only one to interpret satisfactorily all the reactions discussed above, and his formula is now generally accepted.

SYNTHETIC CAMPHOR.

The raw material for the synthesis of camphor is turpentine, the resinous liquid exuding from various *Coniferae*. American turpentine is mostly obtained from *Pinus palustris*, the French variety from *Pinus maritima*, and the Russian from *Pinus sylvestris*. Russian turpentine is not suitable for the manufacture of camphor, on account of its low content of pinene.

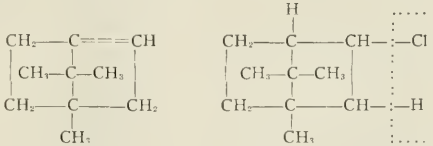
The turpentine is very carefully fractionally distilled, in order to obtain anhydrous pinene ($C_{10}H_{16}$), which boils at about 155° to 160° C., and which should constitute 90 per cent of a good sample of oil of turpentine.

Starting out from pinene, there are a great number of variations in the processes for the preparation of camphor. Hundreds of patents have been taken out.[10] Some of the typical processes will be mentioned here.

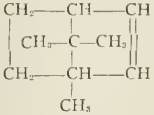
In many of the processes the pinene is thoroughly cooled, and is then saturated with dry hydrochloric acid gas. A white crystalline mass of pinene hydrochloride is thrown out. Pinene hydrochloride is sometimes called "Artificial camphor"—an unfortunate name, for it is still far removed from the true synthetic camphor, and is not suited to the purposes for which true camphor is used.

The next step is to split off hydrochloric acid from the pinene hydrochloride, in order to obtain the hydrocarbon camphene ($C_{10}H_{16}$), which is isomeric with the pinene from which the process started.

The following formulæ indicate the first two steps—the addition of hydrochloric acid to pinene in the position 1.2, and its removal from another part of the molecule, viz., the position 2.3:



(X) Pinene (XI) Pinene hydrochloride



(XII) Camphene

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[9] Bredt and Rosenberg, Annalen der Chemie, 289.

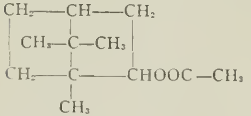
The conversion of pinene hydrochloride to camphene may be accomplished in a great variety of ways, among which may be mentioned:

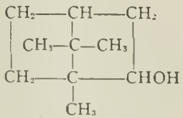
1. Heating with ammonia or with organic bases, such as methylamine, pyridine, quinoline, piperidine, or piperazine.
2. Heating with caustic soda and a salt of a higher fatty acid, such as stearates of sodium, lead, or copper.
3. Heating with phenolates or naphtholates of sodium, potassium, calcium, magnesium, etc.
4. Heating with glacial acetic acid and anhydrous acetates of lead, zinc, or alkaline earth metals.
5. Treatment with magnesium as used in the Grignard reaction.

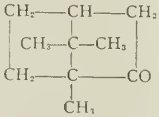
It is worthy of note that camphene is the only solid terpene hydrocarbon. It is a white solid melting at 50° C.

The next stage in the process is the conversion of camphene to bornyl acetate.[11] This is accomplished, as Bertram and Walbaum[12] showed, by treating the solution of the camphene in glacial acetic acid with about 5 per cent of sulphuric acid at a slightly elevated temperature. Acetic acid is added on, in accordance with the formula below. Bornyl acetate is an oil boiling with some decomposition at about 225° C. It is readily volatile in steam.

The final steps in the camphor synthesis consist in the saponification of the bornyl acetate to borneol, and the oxidation of the borneol to camphor.


(XIII) Bornyl acetate


(XIV) Borneol


(XV) Camphor

The saponification is accomplished with alcoholic caustic soda, yielding sodium acetate as a by-product. The borneol so obtained is, with the exception of its optical inactivity, identical with the Borneo camphor occurring in nature.

The oxidation of borneol to camphor can be accomplished by a great variety of oxidizing agents—air, ozone, chlorine, nitric acid, potassium permanganate, potassium bichromate, and sulphuric acid, and finely divided metals such as nickel and cobalt.[13] When potassium bichromate and sulphuric acid are used, chrome alum is obtained as a by-product.

The type of process outlined above thus involves six distinct stages before the final product is obtained: turpentine ⟶ pinene ⟶ pinene hydrochloride ⟶ camphene ⟶ bornyl acetate ⟶ borneol ⟶ camphor.

According to a German process, the anhydrous rectified oil of turpentine is heated directly with anhydrous oxalic acid. Some camphor is formed, and the oxalic and formic esters of pinene, which are also present, are saponified and oxidized. Salicylic acid may also be employed instead of oxalic acid.

The crude camphor obtained by any of these methods is refined by steam distillation or sublimation, in the same manner as the crude natural camphor is purified.

PROPERTIES OF SYNTHETIC CAMPHOR.

Synthetic camphor is identical with the natural article in all its chemical and physical properties, with the exception (in common with other synthetic organic compounds) that it is optically inactive. The question of the differences of physiological action of the dextro, lævo, and synthetic modifications appears not to be settled.[14] The differences seem to be of degree and not of kind.[15] Johnston[16] makes a plea for the recognition of synthetic camphor in the British Pharmacopœia, on the ground of its therapeutic equivalence to natural camphor.

As regards the chemical purity of synthetic camphor, celluloid manufacturers state that it must be quite free from chlorine for use in the preparation of celluloid.

HISTORY AND FUTURE OF CAMPHOR.

The short history of synthetic camphor since it was first made about 10 years ago has been a very troubled one, and the future of the industry still seems to be a matter of great uncertainty. This checkered career has been caused, largely by a great fluctuation in the price of natural camphor. Forty years ago the price of Japanese camphor was about 8 cts. per pound. The Japanese Government assumed a monopoly of camphor in 1899, after the Chino-Japanese War. In 1903 the price was about 30 cts. per pound. At the time of the Russo-Japanese War, in 1905, the price of camphor rose to over a dollar per pound, and in 1906 and 1907 it was about 60 cts. per pound. While camphor was at its highest price chemists succeeded in working out the synthetic processes outlined above, and the manufacture was commenced in Germany, France, and England. In 1909 the Japanese, with large stores on hand, reduced the price of Japanese camphor to about 30 cts. per pound, a price at which it was impossible to manufacture the synthetic article. The French and English companies were unable to overcome financial difficulties, and it is believed that in 1910 only one factory was still making synthetic camphor—the Chemische Fabrik a. A. vorm. E. Schering. The price of cam-

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[10] Cf. O. Kausch, Kunststoffe 4, 1-4, 24-5. F. Rochussen, Chem. Zeitung (1909), 33, 704.

[11] The term bornyl acetate and borneol are used for simplicity. In reality iso-bornyl acetate and iso-borneol are produced. The nature of the isomerism is not clearly understood.

[12] Jour. f. prak. Chem., NF., 49, 1.

[13] Schering, German patents 271147 and 271157. Also patent of Port Chester Chemical Company, New York (1911).

[14] Langgaard and Maass, Therapeut. Monatsh. (1907), 20, 573. Bruni, Gazz. Chem. Ital. (1908), 38, (11), 1. Hamalainen, Skan. Arch. fur Physiol. (1908), 21, 64.

[15] See, e. g., W. E. Grove, Journ. Pharmacol., 1, 445.

[16] Pharm. Journ., 83, 531.

phor at the end of 1910 was about 35 cts. per pound, and the profits from the Formosan monopoly for the fiscal year ending March 31, 1910, amounted to no less than $1,982,966, with a total production of 4,000,000 kilogrammes.[17] During the last four years the price of camphor has not varied greatly, but the outbreak of the present war has resulted in another rapid advance in price to about double the normal value.

Synthetic camphor is now being manufactured in Germany by the Rheinische Kampfer Fabrik in Düsseldorf. How long this company will be able to continue in operation is a matter of conjecture.

When much is being said of the opportunity of American chemical manufacturers to produce materials hitherto imported from Germany, it is gratifying to be able to record that a start is to be made on the manufacture of synthetic camphor in Philadelphia, early in 1915, by the American Camphor Corporation.

As to the future of synthetic camphor, it would be rash to prophesy.

The Japanese Government is now thoroughly alive to the importance of the conservation of camphor trees. Extensive replanting has been commenced, but many years will elapse before these trees will yield camphor. All of the trees in readily accessible locations have been cut down, and, though immense camphor forests still exist, they are in mountainous districts of the interior, inhabited by savage tribes.

Synthetic camphor has had other enemies besides its Oriental rival. The price and supply of turpentine have been subject to considerable variation. The American manufacturer should, however, have less reason than his European competitors to fear a shortage of turpentine.

Then again, a substance may be found capable of replacing camphor in celluloid,[18] or a substitute may be found for celluloid itself. A great many experiments have already been made in this direction, largely on account of the inflammable nature of celluloid, and the work of Cross and Bevan, Knoll and Knoevenagel and others, on the non-inflammable esters of cellulose, may supply a satisfactory substitute for celluloid in the near future.

All of these questions are matters of speculation, which time will answer. In any case, synthetic camphor, whatever its commercial future may be, stands as a splendid example of achievement in the field of chemical synthesis.

The new building which will form the permanent home of the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburgh, will be formally dedicated on Feb. 26th. The building, which was erected at a cost of $350,000, is the gift of Messrs. A. W. and R. B. Mellon, of Pittsburgh.

SODA RECOVERY FROM ESPARTO LYES.*

In the German periodical, *Chemische Apparatur*, Hugo Schröder, of Grimma, gives a description of the process of manufacture of esparto pulp, with particular reference to the economics of soda recovery. The figures recorded are of considerable interest to papermakers in Great Britain, where esparto is largely used as a source of pulp, and the *World's Paper Trade Review* quotes tham at some length.

The writer takes a mill boiling 40 tons of grass per twenty-four hours, yielding 18 tons of pulp with a consumption of 4.2 tons of soda (Na_2O).

Analysis of the lyes from the boilers showed a density of 10.2° tw.; 100 c.c., weighing 105 gm., gave an evaporated residue of 10 gm. This residue had the following composition:

	Per cent.
Water	20.18
Ash	25.17
Combustible matter	54.65
	100.00

The calorific value of this evaporated residue was determined in a calorimetric bomb. Omitting details of the test, it may be stated that the net calorific value, reckoning the water produced to be discharged in the state of vapor, was 2,451 calories per kilo. Since the residue contained 54.65 percent of combustible matter, the calorific value of the organic matters is 4,500 calories.

In this mill the lyes to be evaporated per twenty-four hours consisted of the original boiler lyes at 10.2° Tw. plus wash waters, the second wash being used as a first wash. The feed lyes thus amounted to 222,000 liters at a density of 6.4° Tw. Hence it is calculated that the original boiler lyes amounted to 138, liters, the rest being wash waters. One liter of boiler lye would give 150 grammes of evaporated residue of the above composition; thus 1,000 liters would contain 83 kilos of combustible matter, and 138,000 liters would give 11,455 kilos of combustible matter. Calculated on the combined boiler lyes and wash waters the combustible matter works out at 5.06 percent by weight.

The evaporating system employed is described as follows: The feed lye at a temperature of 70° C. is evaporated in a triple-effect evaporator to a certain degree, such that the heat generated in the furnace will perform the rest of the evaporation. The furnace consists of two parts—a rotary incinerating furnace and a vertical finishing furnace in which the combustion of the carbon is practically completed. The flames from these furnaces pass through a plate evaporator which may be described as a sort of improved Porion. Two shafts fitted with a large number of circular plates or discs revolved so that the plates are partly immersed in the liquor and partly exposed to the hot flue gases. Thus the layer of liquor picked up by the plates is always being evaporated and renewed as the shafts rotate. The partly thickened liquor from the vacuum pan is fed to the plate evaporator, and the evaporation thus continued is completed in the rotary furnace. The draught in the vertical finishing furnace is so adjusted that the carbon is fully burnt without melting the soda.

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[17] Chem. Abst., 1910, 3120.

[18] e. g., German Patent 219918, 1908 (Chem. Fabrik Griesheim Elektron), which covers the use of dioxydiphenylsulphone.

*From Paper.

The writer gives a statement of the heat generated in the furnace and utilized in the plate evaporator.

From the data given above the quantity of feed lye to be treated is 157.75 kilos per minute, with 5.06 percent of combustible matter=7.98 kilos of combustible matter per minute. This is credited with 7.98×5,400 =43.092 calories.*

A utilization of 60 per cent of the available heat is assumed = 43.002 × 0.60 = 25,855 cals. per minute utilized in the plate evaporation.

For evaporating 1 kilo of water from the partly thickened lye from the vacuum pan, including heating it to the boiling point, 580 cals. are required. Thus the combustible matter in the furnace would evaporate 25,855 ÷ 580 = 44.58 kilos of water per minute. Since it was shown above that 105 gm. of original boiler lye yielded 15 gm. of evaporated residue, it is calculated that the furnace has to deal with 13.69 kilos of evaporated residue per minute. To this residue must be added 44.58 kilos of water, which are evaporated in the plate evaporator. The sum, 13.69 + 44.58 = 58.27 kilos, represents the weight of partly thickened lye turned out from the vacuum pan per minute. There entered the system 157.75 kilos of feed lye per minute; thus the vacuum evaporator has to evaporate 157.75—58.27 = 99.48 (say 100) kilos of water per minute. With a feed-liquor density of 6.4° Tw. (1.032 sp. gr.) the density of the lye discharged from the vacuum pan may be calculated thus:

$$\frac{32}{1\ \dfrac{99.48}{157.75}} = 1.0879 \text{ sp. gr.} = 17.6^\circ \text{ Tw.}$$

The arrangement of the triple-effect evaporator was as follows: The heating coils were fed with exhaust steam at a temperature of 106° C. The vapors evolved from the first effect had a temperature of 96° C.; those from the second, 83° C.; those from the third passing to the condenser were at 60° C. A portion of the vapors generated in the first effect was by-passed into a preheater and utilized for heating the feed liquor from a temperature of 70° to 90° C. The rest of the heating, from 90° to 96° C., was done by the coils of the effect.

The results are summarized as follows:

First Effect.

Total heat supplied (by exhaust steam) per minute.26,613 cals.
Water evaporated per minute.................... 33.48 kilos

Second Effect.

Heat supplied by vapors from first effect.........15,333 cals.
Heat supplied by excess temperature of lyes...... 1,616 cals.
16,949 cals.
Water evaporated per minute..................... 30.18 kilos

Third Effect.

Heat supplied by vapors from second effect.......16,949 cals.
Heat supplied by excess temperature of lyes...... 1,868 cals.
18,817 cals.
Water evaporated per minute..................... 33.36 kilos

Total water evaporated in the system 91.71 kilos per minute, with a consumption of 20,613 ÷ 536 = 38.46 kilos of steam. This corresponds to about 5 kilos of good coal per minute, or per twenty-four hours 7.2 tons, but since exhaust steam at scarcely more than atmospheric pressure is employed the cost of the steam is very small.

The soda recovered is 90 percent of 4.2 tons (as Na_2O) = 3.78 tons of Na_2O.

To complete the accounts of the recovery plant there must be credited the heat value of 136 kilos of hot distilled water = about 8,000 cals. per minute. There must also be debited the power consumed in the pumps and rotary plant. These two items approximately balance one another.

GYPSUM DEPOSITS IN BRITISH COLUMBIA.

The Dominion Department of Mines, in a recent report, refers to deposits of gypsum in British Columbia at Spences Bridge, Spatsum, Merritt, Grand Prairie, and North Thompson. The report states that there is a large field open for a good plaster industry in this Province and that the quality of the gypsum found is such that a plaster made from any of the deposits would find ready sale in the rapidly increasing market.

Gypsum was first mined in the Province in 1911, when 500 sacks were shipped to a Portland cement company at Tod Inlet, Vancouver Island. Formerly all gypsum used here was imported from Alaska. The most important of these deposits is that at Grand Prairie, in the Kamloops district, where there is a large bed of pure-grade white gypsum. The Kamloops-Okanagan branch of the Canadian Northern Railway system is located adjacent to the deposit, and the plan is to erect calcining works at Vernon, on the completion of that branch, and calcine and market the manufactured product from that point.

The Spatsum deposit, on the north side of the Thompson River, will be made available to transportation by the Canadian Northern Railway. It has a frontage on the river of about 3,300 feet and covers 450 acres. The mass is stated to be badly disintegrated and highly altered, but a band of pure gypsum 5 feet wide is exposed in the tunnel. The deposit at Merritt is a gypsite, accompanied by selenite or fibrous gypsum. It occurs in a finely divided state, which saves crushing, and forms a quick-setting, strong and reliable plaster, suitable for stucco, as a retarder for cement, and for fertilizer. A similar deposit to that at Merritt is reported from Tulameen.

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*Translator's Note.—There appears to be a clerical error here, by which 5,400 has been written instead of 4,500. The available heat units would seem to be 7.98 × 4,500 = 35,910 calories per minute. This would affect the subsequent results, but not the principle of calculation. Mr. Schröder's figures have been retained in the text.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

Indian Vegetable Tallow.

The U. S. consul at Bombay reports that the war in Europe has been preventing exports from India of the seed of the *Vateria indica* tree, known also as the piney tallow tree, which produces a substance known as vegetable tallow, which formerly found its chief market in Antwerp. This tallow is said to be useful in the manufacture of candles and of soaps and to bring almost the same price as good animal tallow. It is said that after refining it is edible and suitable for use in making confectionery. A firm in Bombay interested in the export of this product, and which desires to have its properties understood by manufacturers in America, has furnished the following information concerning the same:

> It is only of late years that attempts have been made to exploit these seeds and their tallow commercially. The results, however, have been so eminently satisfactory and the prices obtained in Europe for both the seeds and the tallow so favorable that it became evident that the raw product was of exceptional value. This fact has since been confirmed by actual sales of tallow after refining at over £100 ($486.65) per ton in Europe.
>
> The seed is collected in the form of a husked kernel, which, after removal of the husk, is artificially dried, this process generally resulting in the splitting up of the kernel into three or four pieces. In this form it is ready for export. The kernels after drying and treatment by a solvent process yield an average of 30 per cent of their weight of a solid tallow, the constitution of which can be referred to in any standard work on oil seeds. This tallow after refining is edible in the highest degree and, from the prices obtained for it, it must also possess some very special properties. It is said to be largely used in the higher branches of confectionery. It is also perfectly constituted for the manufacture of stearin, glycerin, and olein, but the fact that it is at the same time edible, and consequently commands a higher figure for this purpose, debars it from use in this branch of manufacture.
>
> The price of the dried kernels f. o. b. Bombay packed in gunny bags would be somewhere about $46.17 per ton gross. It is said that in New York this vegetable tallow should sell for about 5 cents per pound.

Coal ar Products Inquiry.

According to the Oil, Paint and Drug Reporter an important announcement has been made by the officials of the Bureau of Foreign and Domestic Commerce having a bearing upon the production in the United States of coal-tar products. This announcement is to the effect that Thomas H. Norton, former United States consul at Chemnitz, Germany, has been appointed a commercial agent of the Department of Commerce to undertake a special investigation of the chemical industry in the United States, particularly in respect to coal-tar products. In commenting on this appointment the officials said:

> It is hoped that his report will be helpful in the development of synthetic dyestuff manufacture in the United States. Those wishing to offer suggestions to Mr. Norton may address him in care of the Bureau of Foreign and Domestic Commerce, Washington, D. C.

It is further said by the bureau officials that Mr. Norton is an expert chemist, and it will be remembered that he made investigations several years ago into the chemical industries of Belgium, the Netherlands, Norway and Sweden. He has written also upon other features of the chemical industry.

Menthol Industry in Japan.

In a recent consular report Max D. Kirjassoff, Deputy Consul General at Yokohama, states that the yield per acre of dried peppermint leaves in Japan ranges from 243 to 375 lbs., varying according to different localities and different years, but the average annual production for the years 1908 and 1912, inclusive, was 321 lbs. per acre. The following table shows the amount and value of the crude peppermint, peppermint oil, and menthol produced in Japan from 1908 to 1912, inclusive:

	Crude peppermint.		Peppermint oil		Menthol.	
Years.	Pounds.	Value.	Pounds.	Value.	Pounds.	Value.
1908..	141,090	$114,570	89,364	$ 93,182	79,268	$107,978
1909..	228,711	248,208	143,317	156,255	149,103	263,096
1910..	248,745	382,430	158,243	177,261	150,413	276,875
1911..	352,960	728,807	165,356	222,887	166,161	495,933
1912..	619,512	1,553,303	208,128	296,537	202,457	999,278

The amount and value of the peppermint oil and menthol are not included in the figures given for the amount and values of crude peppermint.

The cost of the plants is about 12 cts. per 100 lbs., and, as about 495 lbs. of plants are needed for an acre, the cost per acre is 59 cts.

Manganese Supplies Curtailed by the War.

Among the important industries that have been affected by the war in Europe is the production of manganese ore and alloys. The ores are used in the manufacture of glass and dry batteries, and the alloys are essential in the manufacture of steel. In 1913 the United States received from Russia and India about three-fourths of the manganese ore required for domestic use and imported from England and Germany about half the amount of ferromanganese needed by the steel industry. D. F. Hewett, of the United States Geological Survey, who has examined the figures showing the imports of these materials for the first nine months of 1914, states that the receipts of manganese ore have been 42,550 tons, or 16 per cent less and those of ferromanganese 37,420 tons, or 37 per cent less than for the corresponding period in 1913. As the Russian ore is shipped from the ports of Poti and Batum on the Black Sea, through the Bosporus, the entrance of Turkey into the war in October and the consequent closing of the straits to English ships will greatly curtail if not completely stop the export of all Russian ore. It seems probable, therefore, that the receipts of ore during the last three months of 1914 were much less than for the corresponding period in 1913. The imports of ore for the entire year of 1914 were probably at least 25 per cent and of ferromanganese 40 per cent less than for the preceding year.

The rise in prices of ore and ferromanganese reflects the decline in imports. According to the schedule published by the Carnegie Steel Co., this rise ranges from 80 cents to $1 a ton, according to the grade. The price for standard 80 per cent ferromanganese was almost constant at $40 a ton until August. During the few weeks of confusion following the outbreak of the war extraordinary prices reaching as high as $140 a ton were quoted, though it is probable that little was sold at prices above $100 a ton. From August there was a steady decline to $62 a ton until November, and recently the price has risen to $80 a ton. The price of spiegeleisen has shown similar variations but to a less degree, ranging from a minimum of $22 in May to $26 a ton at present.

The effect of this shortage of ore in the United States and the consequent rise in prices has been to stimulate interest in domestic manganese deposits and to cause vigorous development of producing mines. Although several mines previously idle have been reopened, no important new sources appear to have been found. Estimates of production from a few mines only are available, but it is doubtful if the total production of ores for 1914 greatly exceeded if it even equaled that for 1913, which was 4,048 tons. An interesting consequence of the shortage of ferromanganese has been the attempt to establish new reduction plants to use sources of ore hitherto not available. The Noble Electric Steel Co., having access to cheap electric power at Heroult, Cal., is attempting to establish the industry, using ores from Mendocino County. In the East the success of the attempt to make a low-grade ferromanganese from manganiferous iron ores from the Cuyuna range, Minnesota, by the American Manganese Co. at Dunbar, Pa., remains to be established.

The disturbances of the war will make necessary a number of adjustments in the foreign industries using manganese. The English steel industry depends largely on ferromanganese made from Indian and Russian ores, and the supply from India will probably be assured even if the Suez Canal were to fall into the hands of Turkey. Germany, however, with only scanty domestic ore resources, has been importing increasing amounts of ore from the Caucasus in Russia, and large investments of German capital have recently been made in this district. Unless there has been extraordinary foresight in assuring a supply, the continuance of the war for a year or more will make the shortage of manganese ore keenly felt in the German steel industries.

Canadian Feldspar and Plumbago.

During the past four years the exports of Canadian feldspar and plumbago to the United States have become prominent. The mining of feldspar was commenced in the Kingston district in 1890, when the amount mined was 700 tons. The first trial shipment of 50 tons of feldspar in 1893 was not a success. The second shipment, 972 tons, occurred in 1896. This year the amount will reach 16,000 tons. The entire production of Canadian feldspar is from the district about 20 miles north of the city of Kingston. It is used in the large potteries at Trenton, N. J., and East Liverpool, Ohio, and in recent years the cheaper grade has been employed in manufacturing low-grade sand soap.

The plumbago (graphite) mine is located at Calabogie 100 miles to the north of this city on the Kingston & Pembroke Railroad and is operated by an American company. The values of this company's shipments to the United States is $60,000 per annum. In recent years a strong and cheap competitor is the artificial graphite manufactured in electric furnaces at Niagara Falls, Ontario, whose production in 1912 amounted to 2,302,625 lbs. The plumbago exported from Calabogie is chiefly used by the manufacturers of stove polish.

Official returns prepared at Sydney, Australia, show the yield of gold for the State of New South Wales last year to have been 124,507 ounces fine, valued at $2,573,760, as compared with 149,657 ounces, valued at $3,093,648, in 1913.

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THE FUNCTION OF ENZYMES.*

By SAMUEL C. PRESCOTT.

The study of the chemical or physiological activity of cells, whether of microbes or of men, is at once one of the most interesting and one of the most difficult problems of the biologist, for it seeks to disclose the secrets of life processes. How does a disease germ produce its poison, or a yeast cell bring about its characteristic fermentation? How do we carry on those transformations of food material by which beefsteak and bread and butter at once become available sources of energy and matter for our living machine? How does a potato manufacture-starch in its leaves, transfer it to the growing tubers, and there store it up for future use?

In each case by means of enzymes, which we may define as the tools of cells and the reagents by which the chemical reactions of cells of all kinds are effected.

The term "ferments" was first used early in the nineteenth century by Schwann and Berzelius. Afterwards the word was used somewhat indiscriminately, meaning either a micro-organism of fermentation or a chemical substance which in some way was related to living cells. To distinguish between these, the physiologist Kühne suggested the term "enzyme" to designate the digestive ferments such as pepsin, trypsin, and ptyalin. The word has now been universally accepted as the name of a group of chemical bodies, products of living cells, which have the peculiar property of effecting the chemical operations of living matter but which do not enter into the final products of these reactions.

Chemistry cannot produce enzymes, for they are found only as the products of protoplasm of living cells, and it makes no difference whether we are dealing with the ultra-microscopic bacterium or the giant redwood or the whale, the chemical activities are due to enzymes. Furthermore, the same kind of enzyme may be produced by organisms of widely different character, as, for example, the trypsin of certain bacteria, of the carnivorous plants like the Venus Fly Trap, and of the human intestinal tract.

Since the variety of chemical processes carried out by living cells is large in number, it follows that the number of enzymes is legion. Even the number produced by a minute bacterial cell hardly visible with a high power of the microscope may be several, while with organisms of highly specialized form and physiological division of labor the number is greatly increased. In man, at least fourteen are known to be developed in the alimentary canal, and to take part in the process of digestion, while, if we added all the other chemical changes which may be elaborated in the body as a whole, our catalogue would be greatly increased. Moreover, we may assume that there are many enzymes which are still unknown, for the enzymes may be intra-cellular, that is, acting only within the cell, as well as extra-cellular, or extruded outside the cell and so possibly capable of detection. The positive knowledge of the action of intracellular enzymes is still very meagre, although when Büchner discovered zymase and a method for its preparation in 1897, the first great step forward in their study was made.

What an enzyme really is, cannot be exactly stated. An enzyme is known only by its reactions. "By their works ye shall know them," is essentially true in the ferment world. We cannot even tell their composition or to what class of chemical substances they belong, for they have never been obtained in pure condition. It is generally assumed, however, without proof, that enzymes are protein-like in character. In spite of this indefiniteness and the elusive character of these bodies, certain general properties regarding them have become known and on these points all enzymes behave in like manner, although differing distinctly from other chemical substances.

We may thus regard enzymes as forming a special and peculiar group of chemical compounds, differing in certain ways from other substances, and especially in their relation to the law of mass action as shown by the great disproportion between the amount of the active substance and the amount of material changed. A good example of this is rennet, which, it has been stated, can coagulate from 500,000 to 800,000 times its weight of casein without being used up. All enzymes possess the same characteristic but not necessarily in the same degree. The activity is largely dependent upon the physical and chemical conditions of the environment. Thus very slight changes in the reaction of the medium on which an enzyme is acting may control very largely its power, or make the difference between high efficiency and practical inactivity. Some enzymes require neutral solutions for action, others are most vigorous in slightly acid or slightly alkaline media.

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*From American Journal of Pharmacy; reprinted from Science Conspectus, vol. iv, 1914, No. 3, pp. 76-79.

Similarly, temperature may play a very important part in the control of enzyme reactions. In this respect, these substances behave closely like living cells and like certain kinds of proteins. Each enzyme has a maximum, a minimum, and an optimum temperature of activity, just as microbes have, and, like these, if heated above the maximum, will be rendered inactive and finally destroyed. This thermal death point, as it may be called, is very near coagulating point of albumin and not far from the death point of most vegetative bacteria. Another similarity to the proteins lies in the fact that both enzymes and albumins are precipitated by concentrated salt solutions such as ammonium sulphate, by alcohol and by salts of heavy metals. Furthermore, they may be more or less compeltely mechanically precipitated with flocculent or bulky precipitates, as by use of phosphoric acid and lime water. Certain poisons may also inactivate enzymes. Substances which kill living cells, like formaldehyde, hydrocyanic acid, or mercuric chloride, will in general "kill" enzymes, providing the solutions used are strong enough and sufficient time is allowed for the destructive action. The enzyme has a somewhat greater resistance than has the living cell, but the difference is one of degree rather than of kind. In fact, so closely do enzymes correspond to microörganisms in behavior toward physical agencies, poisons, etc., that we use the same terminology in discussing them and speak of the "poisoning" or "killing" of the enzyme. Other substances, such as toluene, chloroform, and a few others, permit enzyme reaction but restrain the activity of living cells, this giving a differentiation of great value in studying them.

Enzymes also have many properties in common with the *toxins*, and, so far as body reactions go, seem to belong to the same class of organic compounds. When a toxin is injected in small amount into the body, certain chemical changes are set up, and there is soon formed a so-called antitoxin which neutralizes or inactivates the toxin. Similarly, the action of enzymes upon the tissues of the living body is effected by the secretion of anti-enzymes, and the injection of foreign proteins into the body may be followed by the manufacture of a "precipitin" which will precipitate that particular protein and no other. This specific action is characteristic of enzymes and toxins as well as of proteins. In view of the fact that enzymes and toxins are, like proteins, the products of living cells, it may not be strange that this similarity is found. However, we are not able to say that enzymes are protein in character, but rather that they are found in association with proteins. The purest enzymes yet prepared do not give protein reactions. Moreover, mineral salts seem essential for their action.

We may explain the mechanism of fermentation and putrefaction changes on the basis of the enzymes, produced by the inciting organisms, for in recent years it has been shown that the enzymes, carefully prepared and fed from living cells, will carry on the same changes with almost mathematical precision. In yeast, for example, Büchner found within the cells an enzyme which could only be extracted by grinding with fine sand and subjecting to enormous pressure, but which, when thus obtained, produced alcohol and carbon dioxide from sugar in exact accordance to the chemical equation which had long been used to represent the fermentation. Thus it was shown that intra-cellular enzymes exist, and we now believe that many processes taking place in living cells—perhaps all the processes—are the results of enzyme activity.

Since the chemical nature of enzymes is so largely unknown, we can classify them only by their action on various compounds. It is possible, however, to group them into the four classes of *hydrolyzing*, or causing the addition of water to certain substances. Most enzymes acting on carbohydrates are of this class. So also are those that affect fats, and the majority of those producing known proteolytic changes. These are best represented in the processes of digestion. A second group are the *Zymase*, or those producing the splitting of bodies into simpler cleavage products without any hydration. The alcoholic fermentation is the best known of this class.

The remaining two classes are the *oxidizing* and *reducing* enzymes, producing the types of change implied. Of the former, the production of vinegar is a familiar example, alcohol being oxidized to acetic acid by an *oxidase* produced by the acetic bacteria. Such familiar changes as the darkening of freshly-cut surfaces of fruits (apples) or the quick change of color when mushrooms and toadstools are broken, also belong to this category. The reduction processes are of enormous variety in nature, both in plant and animal life. While typically distinguished by the reduction of hydrogen peroxide to water and oxygen, these Katalases, as they are called, may also reduce sulphates, nitrates, and various coloring matters, as well as other compounds. Upon the activity of enzymes may depend all the complex series of changes, oxidations, reductions, synthetic and analytic changes which characterize the processes of growth and decay, renovation and destruction in the cell and in tissues. The phenomenon on intra-cellular fermentation seems to be closely linked with enzymic activity, and the building up and breaking down of protoplasm itself is intimately connected with intra-cellular changes and energy liberation.

There is reason to believe that some enzyme actions are like organic chemical reactions, reversible. Thus, maltase will split maltose into two moleculars of dextrose under the ordinary conditions of action. If, however, we add maltase to concentrated dextrose solutions a small amount of maltose (or isomaltose, a similar sugar) will be formed, the reaction proceeding until a certain equilibrium is established. This has not been demonstrated for all enzymes, and some eminent authorities divide enzymes into two classes, only one of which is catalytic and capable of synthesizing as well as splitting substances, while in the other no trace of synthesis has been observed.

On the subject of the origin of enzymes and the causes stimulating their activity many interesting observations have been made. Some enzymes are produced by cells in such form as to require no further aid to render them active. Others require the presence of a specific substance known as an activator. The pepsin of the stomach is produced by the cells of the gastric glands as a zymogen called pepsinogen, which, under the influence of the hydrochloric acid produced at the time the stomach is functioning, becomes changed to pepsin. We do not know how the enzyme and the acid are associated, but we know that the latter is necessary for the production of pepsin and also for its action. Bayliss has described another instance in which the activator itself, enterokinase, acts as an enzyme upon the zymogen, trypsinogen, thus producing trysin, but without entering into the actual formation of the finished enzyme—trypsin. If this view is correct, we have, in effect, one enzyme bringing a second into existence. In other instances, activation is effected by metals, as in the laccase, the oxidizing enzyme of the lac tree of Asia, which requires manganese; or by salts, such as phosphates, as in certain alcoholic fermentations.

In spite of the apparent lack of exact knowledge of the composition of enzymes and of all their activities, we find in this group of substances agents which are of direct and certain application to industrial processes. Bread-making, brewing, cheese-making, certain phases of tanning, as well as the preparation of lacquers and castor oil, are a few of these applications.

Here is a field of great promise and infinite interest, sure to yield results if investigated patiently and consistently by the scientist who combines a deep knowledge of organic chemistry with an intimate acquaintance with cell behavior and activity, and this field of bio-chemistry is sure to find greater favor in the immediate future.

In order to minimize as much as possible the crisis in the Portuguese cotton industry, the Government has issued a decree providing for its guarantee, up to $200,000, of the payment of notes of purchase and sale of raw cotton under certain conditions.

The placing of iron ore on the contraband list by the British Government has had the effect of bringing to Great Britain a heavy tonnage of hematite ore from Spain and Norway, destined for Dutch ports.

THE U. S. BUREAU OF STANDARDS; ITS ORGANIZATION AND ITS FUNCTIONS.

By **S. W. STRATTON**, Director.

Since the Bureau of Standards deals almost entirely with scientific and technical problems, the following brief statement as to its functions and organization may be of assistance to those who are more or less unfamiliar with its work.

The standards with which the Bureau is authorized to deal may be conveniently classed as follows: First, standards of measurement; second, standard value of constants; third, standards of quality, and fourth, standards of mechanical performance.

STANDARDS OF MEASUREMENT.

A standard of length may be taken as an example of a standard of measurement. It must be a length which is unchanging, reproducible, and capable of being compared with the working standards used in the most precise scientific work or with those used in commerce and industry. The fundamental standard must be subdivided and working standards prepared of these parts; for the measurement of greater lengths, standards must be prepared which are multiples of the fundamental standard. This process of subdividing and multiplying the standard involves even more difficulties than those met with in the preparation of the fundamental standard itself. The construction of a set of standard weights from a single unit is also an illustration, but a whole set of standard weights must be prepared before the standard weight of the government can become available to the public. When the standard of length or weight has been found with as many desirable qualities as possible, and before the working standards of the subdivisions or multiples can be prepared, the question as to the method of comparison arises which again involves the solution of difficult scientific problems in connection with the balance or the methods used. These balances range from that capable of measuring the thousandth part of a milligram to the large testing machine capable of measuring a load of thousands of tons. The complete range must be covered, which involves not only a large number of working standards, all of which must agree with the fundamental standard, but apparatus suitable for the comparison of these standards with all of the lengths or weights found in practice.

These steps and equipment are absolutely essential in order to secure uniform measurements of length or weight throughout the country, and they have their counterpart in every quantity that has to be measured, whether it be length, weight, temperature, heat, light, or the various electrical measurements or other standards of measurement. These standards in one form or another are involved in practically every scientific investigation, industrial process, or engineering structure.

PHYSICAL CONSTANTS.

There are many fixed relations between physical quantities, the values of which it is extremely important to know. These values are usually termed physical constants and are used in every branch of scientific work or industry. The amount of heat required to change a pound of water into steam under normal conditions and the relation between heat and mechanical energy are two important physical constants; their values are used in practically every computation in connection with the designing of steam engines and boilers, the tests of their efficiencies or the measurement of their output. The amount of heat required to turn liquid ammonia into vapor or the amount of heat required to melt a pound of ice are constants equally important in the refrigerating industries. The value of the relation between electrical and mechanical energy is involved in many important commercial transactions concerned in electricity. Accurate and authoritative values of these constants are just as essential as in the case of standards of measurement. Many of these now in use are old and obsolete and need re-determination by means of the best modern facilities for physical measurement. Their determination involves the most difficult and precise work in all branches of physics and chemistry,—a fact not generally known by others than those engaged in the scientific and technical work where these constants are used.

STANDARDS OF QUALITY.

A standard of quality for a given material may sometimes take the form of a sample of that material with which other materials of the same kind can be compared; but this is generally a makeshift of the poorest sort. It is only resorted to in the absence of definite and reliable specifications in terms of measureable properties; that is to say, a standard of quality of a material usually takes the form of a specification or definition of its properties, involving, of course, the measurement of those properties by means of the usual standards of measurement. A certain kind of steel, a cement, a paint, an oil, or a paper or cloth, is found by use to be good or poor. The question then arises, —why is it good or poor, what are the physical or chemical properties or the particular combination of elements which make it of good or poor quality, how are its properties to be measured or its constituents determined? These are questions for the laboratory to answer, and involve physical and chemical investigations of the most difficult sort.

A standard of quality for a given material necessarily takes into account the purpose for which the material is to be used; to set the standard too low results in losses, poor efficiency, and even loss of life; to make it too high may result precisely in the same thing; that is to say, the material must be suitable for the purpose intended, and the Bureau's investigations in connection with the properties of materials are to enable the user of these materials, first, to select intelligently the material best suited for the purpose, second, to specify it in terms which the producer cannot mistake, and third, to make the necessary tests to ascertain whether or not the material supplied is in accordance with the specifications.

The actual testing of materials by the Bureau of Standards to ascertain whether or not they comply with specifications, is confined almost exclusively to government purchases, but in making these tests,—in which the Bureau has had the hearty co-operation of practically all the departments of the government service,—it is compelled to make many investigations concerning the properties of materials, their specification and measurement. While this work is of great value in placing government purchases on a correct business basis, the results of the investigations as to the properties of materials and the information gained in testing government supplies is even more important to the general public, and is distributed in the form of suitable publications.

The Bureau does not compete with private testing laboratories, but endeavors to assist them by the development of standard specifications, methods of measurement, and other matters where uniformity is desirable, much of which information, as stated above, is secured in connection with the testing of materials purchased by the government and a close observation of their use.

The time is not far distant when it will be required that all materials bought or sold shall be as represented, but it should be kept in mind that this is impossible except in the case of those materials where proper standards of quality and methods of measurement have been developed. It must not be assumed that the purchaser or user is the party principally benefited in the development of such standards; on the contrary, the manufacturer, first of all, is interested in the quality and all things which affect the quality of his product, and while the Bureau's efforts in this field are devoted principally to the pointing out and measurement of those properties upon which the quality of the materials depend, it is to be regretted that its force and equipment is insufficient to render more assistance to manufacturers with a view to a direct improvement of those parts of the process upon which the quality of the output depends.

STANDARDS OF PERFORMANCE.

The value of an instrument, device, or machine, almost always depends upon the efficiency of its performance. In such cases it is necessary to state the performance desired or guaranteed in terms which are correct and susceptible of measurement. As in the case of standards of quality, the standard involved is more often in the form of a specification, but specifications are useless based upon correct scientific and mechanical principles and supplemented with a statement of the method to be used in ascertaining whether or not the specifications or guarantees have been complied with. The performance of an engine or boiler, a pump, an electrical generator or motor, a weighing device, or a telescope, can usually be measured, but the quantities to be measured and the method used must be specified correctly and understood by all the parties concerned in the construction, purchase, or use of such apparatus. To do this properly involves the use of standards of measurement, standard values of constants, and standards of quality. The Bureau of Standards does not attempt to cover this field completely, but only those cases where there is a lack of definite information upon which to base specifications and only to the move important classes of apparatus. To secure this information involves investigations quite as scientific in character and as difficult as in the case of other standards, as well as a knowledge of technical and manufacturing processes.

The Bureau's activities in this field have only been developed to a slight extent and almost entirely in connection with government purchases. It has had in this, as well as in the field of the properties of materials, the most hearty co-operation of the various government experts, manufacturers, engineers, and technical societies.

Government purchases are not greatly different from those of the public; whenever the Bureau makes a scientific investigation or secures information from other sources for the purpose of the improvement of specifications used in connection with government purchases, whether for measuring instruments, or for materials or equipment, such information or data is given to the public in the form of suitable publications. The value of this information from the standpoint of the public is even greater than that in connection with government purchases, important as the latter is. In other words, the needs of the public and the government service are precisely the same as far as standards or specifications are concerned, whether it be standards of measurement, quality, or performance. In the case of the public, the Bureau confines its work to those investigations, experimental or otherwise, which enable it to give intelligent advice regarding the use, purchase, and testing of the more important apparatus and materials, leaving the testing to commercial laboratories; except, of course, in the case of standards of measurement, where it is absolutely essential that the standards of the public be compared with those of the government to secure uniformity of measurement, and in unusual cases of testing where the public is not yet provided with suitable means of equipment. In the case of the government, the Bureau goes father and serves as a testing bureau for the various departments when called upon, and as such is assisting to place government purchases upon an economical and business-like basis. The example of the government in such matters has a far greater influence upon the public than most people suppose; the government can do no greater service to the country than to place its own purchases on a basis which may be taken as a standard by the public at large.

RELATION OF THE BUREAU'S WORK TO THE PUBLIC.

It is perfectly obvious, even to one unfamiliar with the subject, that the maintenance on the part of the government of correct standards of measurement or quality or performance calls for continuous scientific and technical investigations of the highest grade, involving the most competent expert services and the best scientific equipment. When this is accomplished, there still remains the serious problem of making the results available and useful to the public.

The Bureau compares with its own standards of measurement the standards or measuring instruments of states, cities, scientific laboratories, educational institutions, manufacturers, government bureaus, or the public, for which a nominal fee is charged, except in the case of the national and state government institutions. It gives advice concerning these standards or their use, whether it be in connection with the enactment of laws, regulations, or ordinances concerning the weights and measures of every-day trade or in connection with precision standards used in scientific work and the industries. It gives advice upon request to state and city officials, public service commissions, public utility corporations, regarding the standards of measurement, of quality or performance, involved in legislation or regulation pertaining to the public utilities. Many questions of disagreement between the public and utility companies as to these matters are referred to the Bureau for advice or adjustment, often avoiding unfair or inconsistent regulations, as well as long-drawn-out and expensive litigation. There is a great need on the part of the public for unbiased and reliable information pertaining to the standards entering into the regulation and sale of the services of public utilities. As far as possible such information is given in the form of publications upon definite subjects.

It must not be inferred from the above that the Bureau's activities are devoted principally to the interests of the user or consumer. The fundamental facts regarding standards of measurement, quality or performance, are the very things which most deeply concern manufacturers; they are fundamentally concerned, either directly or indirectly, with the improvement of methods of production or the quality of the output. It may be said that the Bureau occupies somewhat the same position with respect to the manufacturing interests of this country that the bureaus of the Agricultural Department do to the agricultural interests. Many industries are just beginning to realize the importance of precise methods of measurement and scientific investigation, which, in practically every case, involve some kind of measurement.

It is upon quality as well as upon price that competition must finally depend, whether in domestic or foreign commerce. The use of exact methods and scientific results is the greatest factor in the improvement of quality, efficiency, or the development of new industries. The educational value of the Bureau's work in this respect is almost entirely unknown to the general public and yet the Bureau receives hundreds of letters, as well as many personal visits from manufacturers, seeking information as to standards of measurement, how to use them, how to measure the properties of materials, or as to the fundamental physical and chemical principles involved; also, what is of even greater importance, how to initiate and carry out scientific investigations and tests on their own account in their particular fields of work.

ORGANIZATION.

The organization of the Bureau's scientific and technical staff is based upon the nature of the expert service involved rather than upon the classes of standards. For example, the Division of Weights and Measures has to do with all matters pertaining to standards of length, mass (weight, as it is commonly termed), time, density, and similar questions, whether they arise in connection with the precision standards used in scientific investigation, the master standards of manufacturers, or the ordinary weights and measures of trade. A standard of quality or performance where any of the above measurements form the fundamental and most important factor would be referred to this division.

The Division of Heat and Thermometry has to do with heat standards, and testing of heat measuring apparatus, the determination of heat constants, of which there are many, and all investigations pertaining to quality or performance where heat measurement is the essential and predominating factor.

Similarly, the Electrical Division is concerned with all the electrical problems that may be taken up at the Bureau, whether in connection with the various electrical standards of measurement, electrical constants, the electrical properties of materials, or the performance of electrical equipment.

Questions in optics enter into standards of all kinds to a greater extent than has been supposed; hence, there is an Optical Division provided, with experts in spectroscopy, polarimetry (used in sugar analysis), color measurement, the principles of optical instruments, and the measurement of the optical properties of materials.

Practically all investigations concerning the various classes of standards involve chemistry in one form or another. There are also many chemical standards and questions which arise in connection with chemical work generally, especially in the industries; hence, there is a Chemical Division, co-operating with every other division of the Bureau, as well as taking care of the questions of a purely chemical nature that come to the Bureau and which fall within its functions.

In the case of the more important technical fields, divisions have been formed dealing more specifically with large and important classes of materials, but many of the purely scientific questions involved would be handled by one of the above scientific divisions or jointly with it. The work of the technical divisions is just as scientific in character, but deals more specifically with manufactured products.

The work of the Structural Engineering and Miscellaneous Materials Division includes the investigation, testing, and preparation of specifications for the above materials, such as the metals and their alloys, stone, cement, concrete, lime, the clay products, paints, oils, paper, textiles, rubber, and other miscellaneous materials.

The Division of Engineering Research makes investigations and tests regarding the performance and efficiency of such instruments, devices, or machinery, as the Bureau may take up and do not fall directly under one of the scientific divisions. The division is a small one and its work is devoted almost exclusively to assistance given other departments of the government and the General Supply Committee in designing, specifying, or testing equipment. It should in time form one of the most important branches of the Bureau's work.

The questions pertaining to the manufacture, specifications, testing and use of the metals and their alloys have become so important that a division known as the Metallurgical Division has been formed of the experts engaged in these problems.

The employes engaged in clerical work, purchasing, files, records, accounting and library, are known as the Office Division, while those employed in the operation of the mechanical plant, the various shops, and the care of the buildings and grounds, form the Engineering and Construction Division.

LOCATION.

The laboratories of the Bureau of Standards are located in the northwest section of Washington, on Pierce Mill Road, near Connecticut Avenue, and are reached by the Chevy Chase car line. It was located outside of the business center of Washington in order to ensure freedom from mechanical, electrical, and other disturbances common to the business and more thickly populated sections of the city. Furthermore, the area of ground necessary precluded a site near the city. It has been found by experience that the efficiency of the employes, especially those engaged in testing and scientific investigation, has been greatly increased by the location of the laboratories in a section free from the ordinary disturbances of city life.

During the year 1914 the production of the Ombilien coal mines (Government coal mines of Sumatra) amounted to 440,005 tons, and the production of the Banca tin mines (Government tin mines of the island of Banca) amounted to about 15,319 short tons.

The exports of cotton manufactures from Japan in 1913 were nearly 30 per cent greater than in 1912 and considerably exceeded all previous records in the history of the textile industry of the country.

CHEMISTRY OF THE INCANDESCENT GAS MANTLE.*

By DR. H. S. MINER.

Since the wonderful and spectacular invention of Dr. Karl Auer von Welsbach, who about 30 years ago produced the incandescent gas mantle which in justice bears his name, the growth of the industry has been marked by steady improvements rather than revolutionary changes, unless we include that radical change in the composition of the mantle body which Dr. Auer himself made in the early nineties, when he substituted the thorium-cerium mixture for the more complex lanthanum-zirconium-cerium mantle. This was a radical improvement, and it marked the beginning of the general adoption of the incandescent gas mantle.

I have said that the days of *radical* developments seem to be past, and yet I never cease to wonder at the phenomenon of the change or petrifaction of the vegetable or organic fibre, reproducing the cellulose fibre in mineral form under the influence of the Bunsen flame and giving the light-producing body with which we are familiar. Although we hear the fragility of the mantle frequently alluded to, when I watch its formation in this manner, which seems to be essential to its light-giving efficiency, its strength and resiliency is a "nine days' wonder" to me.

This change in the composition of the Welsbach mantle when the mixture of 99 parts of thoria and 1 part of ceria was substituted for the earlier mixture, is to my mind an invention of the highest type, involving as it did the purification of rare earth materials beyond the limits of previous knowledge, and the development of commercial processes for their production in the highest state of purity.

Notwithstanding the claims made by many *pseudo* inventors, the thorium-cerium mixture still holds as the essential composition of all Welsbach mantles, and is the basis of the light-giving qualities of the incandescent gas mantle. Although the last quarter of a century has brought much enlightenment in the field of rare earth chemistry, no satisfactory substitute has been found for this invention of Dr. Auer's. In justice to the many rare-earth chemists throughout the world, I would say that their work has resulted in some changes and improvements in the mantle and burner which have decreased its cost and increased its efficiency and durability. Some of these points I will touch upon.

In the early days a purified cotton fabric was saturated with the thorium-cerium mixture made of materials of as high a state of purity as possible. Purity of the cellulose was found to be absolutely essential, and bleeching and washing processes were carried beyond the point previously thought necessary, and a cotton carrying less mineral substance than the best absorbent cotton was produced. Realizing the deleterious influence of foreign substances, such as silica, lime, magnesia, alumina, phosphuric acid, etc., it was recognized that it was just as harmful to have these elements brought to the mantle by the vegetable fibre as from a rare-earth mixture. It was recognized that the length of fiber or staple of the mantle fabric had much to do with its physical strength and durability. Long staple cottons were used exclusively in the best grade of goods, and the longer fibered ramie or China grass was looked upon with favor, but was not used with any success until it had been successfully de-gummed, bleached and washed. The accomplishment of this complex and difficult problem resulted in the adoptión of ramie as a mantle fiber, first in Germany and then in other countries. The adoption of ramie fiber made possible the mantle of the inverted or pendant type, which has since been so generally adopted. Although the fiber length was increased from 1½ or 1¾ ins. to 5 or 6 ins. by the substitution of ramie for cotton, and with certain advantages, especially in inverted mantles, yet the ideal had not been reached, and it remained for the artificial silk or artificial cellulose fibers to supply that idea. The slow development of the artificial silk industry caused a delay in the adoption of artificial fibers for mantle making, but its strength, elasticity and maintained candle power have caused a persistance of effort that now has its reward in the arti-fiber mantle.

In the early days the only digressions from the ideal composition of 99 per cent ThO_2 and 1 per cent CeO, were slight variations in these figures to produce lights with varying degrees of whiteness; an increase or decrease of ceria increasing or decreasing the yellow color of the light. The coming of ramie fiber and the inverted type of mantle made the introduction of small percentages of hardening materials essential, and beryllium oxide was found to be an ideal substance for this purpose.

The change of fiber and of the type of mantles, as indicated, has caused a complete revolution in the processes of manufacture, and notwithstanding the experience already gained, each one of these changes called forth persistent research work over a period of years before the problem could be considered solved. This is especially true of the arti-fiber mantles, and the changes in manufacturing processes have extended to the collodion or lacquer used to strengthen the mantle for transportation, as that used on the cotton or ramie mantles was found unsuited for arti-fiber mantles. The problem of primary importance for the chemical engineer has ever been the manufacture of thorium nitrate, and many changes in the commercial production of this substance have been effected during the score of years just passed. Monazite sand is still the only commercial ore from which thoria can be obtained, containing from 5 per cent to 6 per cent ThO_2; although small deposits of thorite and thorianite with a thoria content of 50 per cent and 75 per cent respectively have served to keep alive a longing for a more ideal source of supply. The high price of monazite—this very low-grade ore from a thoria standpoint, with nearly 95 per cent waste—has thrown upon the thoria content, while still locked up in this phosphate rock, a heavy burden of expense and has made necessary the production of high yields and low costs of operation to keep the costs of thorium salts low enough to make them commercially available.

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*From American Gas Light Journal; abstract of a paper read before New York Section, Electro-Chemical Society.

The first processes used in factory practice were naturally but enlargements of laboratory methods of analysis, but from this beginning have developed modification upon modification, substituting cheaper and cheaper reagents and methods of manipulation until the commercial processes of today hardly bear even a "family resemblance" to the first process employed. Modifications are, of course, continuing, and are made imperative by fluctuations in price of the ore, of some reagent, or of labor. But although there be variations in processes, there must be one unvarying standard ever before the chemist, the absolute purity of the product. Pure thoria is essential, and I am gratified to be able to say for the thoria manufacturers of the world that their product is of very high grade and is better now, notwithstanding the cheapening and shortening of processes, than it was in the beginning, although even then it was truthfully labeled "C. P." There are various chemical and physical means of checking and determining the purity of the product, but in the light of experience the most satisfactory method for both accuracy and rapidity is the manufacture of mantles from the thoria as it progresses in purity. The color of the mantle body, the color of the light produced, the presence or absence of shrinkage, the brittleness or flexibility of the mantle give to the experienced manufacturer a more satisfactory indication of the purity of the product than do chemical analyses, which are of necessity long and tedious.

The other essential material which must always accompany thoria is ceria, and although it is used in only about one-hundredth the quantity its chemistry is just as important and its purity just as essential. I am glad to say that this product is even purer than when Dr. Auer first used it in his lanthanum-zirconium-cerium mantle. The oxide of cerium then obtained was of a reddish-brown tint, while that now manufactured is of a light yellow color, the former being slightly contaminated with neodymium, the last traces of which were difficult to remove. By way of variety the mantle chemist has also to manufacture beryllium, zirconium, and neodymium, each of which he uses in a limited way, and none of them are really easy to produce.

Radio-chemistry has recently thrown the thoria manufacturer into the "limelight" because of a radio-active product three hundred times stronger than radium, which occurs in and is produced from thorium. I refer to meso-thorium, which a suffering and stricken humanity has implored the thoria manufacturers to save for them, and which the manufacturers are now unitedly conserving as a substitute for radium.

With the possible exception of the meso-thorium, every problem we have mentioned has a bearing upon the characteristics and qualities of some or all types of incandescent gas mantles. Another and no less important problem that should be alluded to is the protective coating that must be applied to a finished mantle to strengthen it for transportation. In the early part of 1888 we were dipping finished mantles in an alcoholic solution of shellac, made slightly flexible when dry by the addition of a little castor oil. Some essayed to strengthen the mantle with paraffine, and I have in my collection of curios a mantle imbedded in a cake of paraffine, which was to be removed by melting the wax. The making of solutions of nitro-cellulose or soluble cotton opened up a new field of research, and the knowledge gained of the many various forms of nitro-cellulose and the numerous solvents therefor, together with the knowledge and control of such characteristics as vicosity, hydroscopic effects, etc., have made it possible to prepare collodion solutions of almost ideal qualities for mantle purposes. And what are these ideals? A collodion must be of the proper viscosity for mantles to be dipped and withdrawn from it without rupture or strain; it must dry quickly with a film stiff enough for the mantle to be handled with safety, and strong and elastic enough to resist handling and shock; it must burn off slowly enough to prevent the mantle becoming annealed or softened, and yet must not leave the mantle body sticking to the cap of the burner. A collodion which answers all these characteristics is realized in a nitro-cellulose solution in a mixture of solvents with camphor, made flexible by castor oil.

The mantle manufacturer has held before himself for a quarter of a century and more, certain ideals towards which he has earnestly striven. Some of these have been strength with elasticity, high and maintained candle-power, preservation of color, and absence of shrinkage. A realization of these seems finally to have been met in the mantle made from the bundle of elastic, spring-like fibers known as artificial silk, for the strength of these mantles certainly is phenomenal, the high initial candlepower is not only maintained but frequently *increases*. This is made possible by the practical absence of shrinkage upon prolonged burning, and by the very curious phenomena that the mantle does not seem to collect the fine mineral dust from the atmosphere as do those manufactured from the shorter vegetable fibers, cotton and ramie, this silicious dust having a great affinity for the basic materials of the mantle body.

The attainment of this idea has been reached only after years of persistent research, guided by many more years of experience in mantle manufacture. Old theories had to be abandoned and former methods completely changed before this mantle was commercially possible. It was a chemical problem of great complexity, and its successful solution arouses such enthusiasm that I am tempted to include this among the radical and spectacular developments in our industry.

I have described some of the chemical problems connected with the manufacture of the incandescent gas mantle. There are many more that have to deal with the process of manufacture of the mantle itself and with the economics of the industry, such as the conservation and recovery of waste product. My chief excuse of treating the subject as I have done is to make it clear that each new type of mantle developed is an independent chemical problem, beginning with the fiber of which it is formed, through every process and stage of manufacture, to the special collodion with which it is prepared for transportation. I hope I have also shown you that chemistry is just as essential for the successful operation of the incandescent mantle industry as it was in its inception and development.

RUBBER SHIPMENTS FROM AMAZON VALLEY.

The effect of the European war on rubber shipments from Brazil is easily seen in Table I abstracted from the Daily Commerce Reports which gives the exports for December, 1914, and comparative totals for 1913.

TABLE I.

Ports.	Fine. Pounds.	Medium. Pounds.	Coarse. Pounds.	Caucho. Pounds.	Total. Pounds.
From Para to—					
United States	2,814,857	240,718	1,497,410	259,788	4,812,773
Europe	146,771	....	18,188	3,704	168,663
Italy	78,447	7,654	2,017	....	88,118
From Manaos to—					
United States	2,595,497	447,082	521,539	284,617	3,848,735
Europe	285,335	44,816	53,217	57,448	440,816
From Itacoatiara to—					
United States	47,289	2,976	21,550	1,653	73,468
Europe	....	....	....	....	....
Total to United States, December, 1914	5,457,643	690,776	2,040,499	546,058	8,734,976
Total to Europe, December, 1914	510,533	52,470	73,422	61,152	697,597
Total to United States, December, 1913	3,250,118	600,173	1,576,129	582,172	6,008,592
Total to Europe, December, 1913	2,844,269	211,179	734,362	1,070,726	4,860,536
Grand total, December, 1914	5,968,196	743,246	2,113,921	607,210	9,432,573
Grand total, December, 1913	6,004,387	811,352	2,310,491	1,652,898	10,869,128

As the foregoing figures show, there was a drop of 4,162,939 lbs. in shipment of Brazilian rubber to Europe in the month under review when contrasted with exports during December, 1913, and a decline of 1,436,555 lbs. in total exports for the month, notwithstanding the fact that sales to the United Sates advanced by 2,726,384 lbs.

When considering the calendar year 1914 as a whole similar trade changes are to be noted—shipments to the United States advancing 8,491,007 lbs., those to Europe declining 13,978,568 lbs., and the total exports showing a falling off of 5,487,561 lbs. These figures include exports from the Peruvian port of Iquitos. In detail the year's shipments were as shown in Table II.

TABLE II.

Ports.	Fine. Pounds.	Medium. Pounds.	Coarse. Pounds.	Caucho. Pounds.	Total. Pounds.
From Para to—					
United States	11,248,407	1,714,195	9,218,782	5,660,198	27,841,582
Europe	11,386,218	988,636	1,386,322	4,212,722	17,973,898
From Manaos to—					
United States	9,870,156	1,861,713	2,765,006	3,056,153	17,553,028
Europe	7,691,654	1,417,358	1,566,706	4,145,640	14,821,358
From Itacoatiara to—					
United States	129,729	7,919	54,223	19,842	211,713
Europe	92,272	10,009	58,469	40,605	201,355
From Iquitos (Peru) to—					
United States	338,048	45,563	95,797	915,291	1,394,699
Europe	396,197	33,411	170,426	1,467,324	2,067,358
Total to United States, 1914	21,586,340	3,629,390	12,133,808	9,651,484	47,001,022
Total to Europe, 1914	19,566,341	2,449,414	3,181,923	9,866,291	35,063,969
Total to United States, 1913	16,085,220	3,058,102	12,151,590	7,215,103	38,510,015
Total to Europe, 1913	25,615,414	3,537,826	5,169,523	14,719,774	49,042,537
Grand total, 1914	41,152,681	6,078,804	15,315,731	19,517,775	82,064,991
Grand total, 1913	41,700,634	6,595,928	17,321,113	21,934,877	87,552,552

Great Britain has adopted the metric system in the new British Pharmacopœia. This is the official formulary for medicine and pharmacy. The action was taken by the British Medical Council, which is a representative but not a Government body. The effect will be that prescriptions will have the quantities expressed in metric terms. The system is optional with the retailer. As the strength of drugs as well as quantities are now expressed metrically, the druggists will order from the wholesaler in these terms. The pharmacopœias of practically all countries, including the United States, are now in the international metric system.

BARITE OF THE APPALACHIAN STATES.*

By **THOMAS L. WATSON** and **J. SHARSHALL GRASTY.**

INTRODUCTION.

The users of barite in the United States derive their supply partly from the domestic production and partly from the imports from foreign countries. According to the Mineral Resource division of the U. S. Geological Survey, the domestic production of barite in 1913 was 45,298 short tons, valued at $156,275, or $3.45 a ton, and the imports of crude barite were 35,840 short tons, valued at $61,409, or $1.71 a ton. These figures clearly show a decided advantage in cost of the foreign over the domestic barite to users in the United States. The difference in cost is the only advantage to the consumer of foreign barite, for there are large reserves of the mineral in the United States of good grade. The production of many of the operating mines is capable of decided increase, and it is believed that the operating mines together with the large reserves of undeveloped deposits of barite are entirely adequate to meet the demands of the users in the United States.

Deposits of barite are known in California, Idaho, Nevada, and Alaska, but most of them are undeveloped because there is, apparently, no market for the material in that region. The domestic production is derived from Missouri and the Appalachian States, the greater part being obtained from Missouri.

Following the outbreak of war in Europe many users of foreign barite in the United States have been forced to seek their supplies at home. It seems opportune at this time, therefore, that a general review be given of the barite industry in the Appalachian States, one of the two areas from which the domestic supply of the mineral is derived, and that attention be directed to the undeveloped deposits in the region. Briefly, then, this paper reviews the barite industry in the Appalachian States, and describes the occurrence, preparation, and uses of the mineral.

GENERAL CHARACTER.

Barite, known commercially as barytes or heavy spar, is barium sulphate ($BaSO_4$), containing when pure BaO, 65.7 per cent, and SO_3, 34.3 per cent. The specific gravity is 4.3 to 4.6, and the hardness 2.5 to 3.5. The hardness is about that of calcite, but barite can be readily distinguished from calcite by its greater specific gravity and by not effervescing with acids. The mineral is usually white, but it is often found stained red, pink, or yellow by iron oxide. It is usually crystalline, opaque to translucent, and occurs in a variety of forms, commonly as aggregates of straight and slightly curved cleavable plates, as granular, fibrous, and earthy masses, and as single and clustered crystals. It is rarely found pure in workable deposits, the common impurities being silica, lime, magnesia, and the oxides of iron and aluminum. In many deposits galena and fluorite are associated with the mineral. The minable material will usually carry from 95 to 98 per cent barium sulphate.

PRODUCTION.[1]

During the 10-year period 1904 to 1913, inclusive, the production of barite has been entirely from the following states, arranged alphabetically and without reference to order of production: Alabama, Georgia, Kentucky, Missouri, North Carolina, South Carolina, Tennessee, and Virginia. Not all of these, however, have produced during the same year. In 1913, the production came from Missouri, North Carolina, Virginia, Georgia, and South Carolina. The Kentucky deposits did not produce in 1912 or 1913.

The following table gives the total production of crude barite in the Appalachian States and in the United States in short tons from 1904 to 1913, inclusive:

PRODUCTION OF BARITE.

	Total Production,[a] Appalachian States.		Total Production,[b] United States.	
	Quantity.	Value.	Quantity.	Value.
1904	40,229	$ 99,106	65,727	$174,958
1905	21,474	64,705	48,235	148,803
1906	21,362	66,888	50,231	160,367
1907	45,582	129,318	89,621	291,777
1908	22,208	63,674	38,527	120,442
1909	27,130	89,919	61,945	209,737
1910	19,997	46,148	42,975	121,746
1911	16,945	41,412	38,445	122,792
1912	12,918	36,278	37,478	153,313
1913	14,167	38,637	45,298	156,275

[a] Includes Virginia, North Carolina, South Carolina, Georgia, Tennessee, Kentucky, and Alabama.

[b] Includes all states under ([a]) and Missouri.

AVERAGE PRICE PER TON.

	Missouri.	North Carolina.	Tennessee.	Virginia.	Other States.	Total.
1905	$3.14	$3.90	$1.62	$4.30	.....	$3.08
1906	3.24	....	1.67	3.85	$2.94[a]	3.19
1907	3.09	3.76	1.78	3.55	4.18[a]	3.26
1908	3.48	....	1.43	....	3.51[b]	3.13
1909	3.44	....	....	....	3.31[c]	3.39
1910	3.29	....	1.54	....	2.55[d]	2.83
1911	3.79	....	2.27[e]	....	2.63[f]	3.19
1912	4.77	....	2.34[e]	....	2.99[g]	4.09
1913	3.78	....	1.70	....	2.91[h]	3.45

[a] Includes Alabama, Kentucky, Georgia.

[b] Includes Georgia, North Carolina, and Virginia; Kentucky was $4.11.

[c] Includes Georgia, Kentucky, North Carolina, Tennessee and Virginia.

[d] Includes Georgia, Kentucky, North Carolina and Virginia.

[e] Includes Tennessee and Kentucky.

[f] Includes Georgia, North Carolina, South Carolina and Virginia.

[g] Includes Georgia, North Carolina and Virginia.

[h] Includes Georgia, North Carolina, South Carolina and Virginia.

IMPORTS.

The subjoined table gives the imports of barite for consumption during the last 10 years, from 1904 to 1913, inclusive.

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*From Transactions of American Institute of Mining Engineers.

[1] Unless otherwise stated, all statistical data given in this paper are taken from Mineral Resources of the United States, U. S. Geological Survey.

BARITE IMPORTED INTO THE UNITED STATES, 1904 TO 1913, IN SHORT TONS.

	—Manufactured—		—Unmanufactured—		Total
	Quantity.	Value.	Quantity.	Value.	Value
1904.......	6,630	$48,658	7,492	$27,363	$ 76,021
1905.......	4,803	39,803	14,256	62,459	101,262
1906.......	4,807	37,296	9,190	27,584	64,880
1907.......	11,207	96,542	20,544	76,883	173,425
1908.......	3,401	29,168	13,661	58,822	87,990
1909.......	3,016	25,679	11,647	29,028	54,707
1910.......	3,565	29,782	21,270	48,457	78,249
1911.......	3,147	22,083	20,214	36,643	58,726
1912.......	3,679	26,848	26,186	52,467	79,315
1913.......	5,463	38,155	35,840	61,409	99,564

The total yearly value of the imports of barium compounds, 1904 to 1913, including barium carbonate (witherite), barium binoxide, barium chloride, and blanc fixe or artificial barium sulphate, follows:

TOTAL VALUE OF IMPORTS OF BAVARIAN COMPOUNDS, 1904 TO 1913.

Year.	Value.
1904	$242,804
1905	257,427
1906	335,011
1907	357,117
1908	319,114
1909	399,376
1910	470,449
1911	398,213
1912	376,017
1913	391,470

The mineral witherite (barium carbonate) is admitted free of duty but under the Underwood tariff the manufactured barium carbonate is dutiable at 15 per cent *ad valorem*, the natural barite at 15 per cent *ad valorem*, the artificial barium sulphate or blanc fixe at 20 per cent *ad valorem*, barium binoxide at 1½ cts. a pound, and barium chloride at ¼ ct. a pound. On raw barite the duty is $1.50 per ton, on prepared or manufactured barite $5.25 per ton, and on blanc fixe or artificially prepared barium sulphate the duty is ½ ct. per pound.

GEOGRAPHIC AND GEOLOGIC DISTRIBUTION.

Barite has rather wide geographic distribution in the Appalachian States and occurrences of the mineral are known in each of the major physiographic divisions of the region: (1) The Piedmont Plateau. (2) the Appalachian Mountains, (3) the Appalachian Valley, (4) the Cumberland Plateaus, and (5) the Interior Lowlands. It is found in workable quantity in many localities within the Appalachian States, but in recent years the sources of supply have been from Virginia, North Carolina, South Carolina, Georgia, Tennessee, and Kentucky. Deposits of the mineral are also known in Alabama, Maryland, and Pennsylvania. Practically the entire domestic production of the mineral comes from Missouri and the Appalachian States, the former supplying about 65 per cent of the total production.

Geologically, the barite deposits of the Appalachian States are associated with rocks which range from pre-Cambrian to Triassic in age, but the exact age of the deposits themselves is unknown.

The age of the rocks in which the barite deposits are found may be tabulated as follows:

1. Triassic: Virginia.
2. Carboniferous (Mississippian): Western Kentucky.
3. Cambro-Ordovician: Central Kentucky, Tennessee, Appalachian Valley region of Virginia, Georgia, Alabama, Maryland and Pennsylvania.
4. Pre-Cambrian and Cambrian: Piedmont Plateau province of Virginia and North Carolina, including the Madison County deposits in the western part of the State.

Of these four horizons, the Cambro-Ordovician is vastly the most important in the Appalachian States and to it belong the deposits of Missouri, the principal producing area in the United States. The deposits of barite concentrated in the residual clays derived by weathering from the rocks of the several horizons tabulated above are later in age, probably much later.

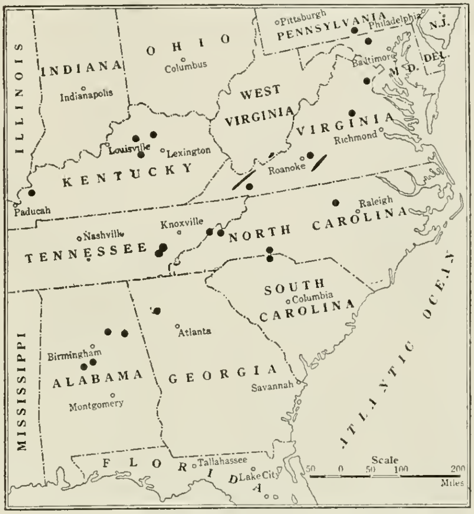

Fig. 1. Barite Deposits in Appalachian States.

MODE OF OCCURRENCE.

Barite is not a pyrogenetic mineral, nor is it known in contact-metamorphic deposits, in pegmatite veins or dikes, or as a product of dynamo-regional metamorphism. It is a common mineral, however, in many kinds of rocks—igneous, sedimentary, and metamorphic, and in nearly all if not in all cases it was formed by deposition from aqueous solutions. Many writers record the deposition of barite from spring and mine waters of carbonate and even sulphate composition, but especially sodium chloride waters.[2] Depositions from both hot and cold water are recorded.

Thus far, therefore, the occurrence of barite is limited to deposits of moderate and shallow depth, either nearby, sometimes in, or removed from igneous rocks, but not formed, according to Emmons,[3] in deposits of the deep-vein zone.

The occurrences of barite in deposits of sufficient concentration to be of commercial value are (1) as veins, (2) as replacements of limestone, and (3) as a residual mineral in clays resulting from weathering.

Vein occurrences of the mineral may include (1) barite as a common gangue mineral in veins of metallic ores; or (2) barite as the chief mineral in veins, with little or essentially no development of metallic ores, in sedimentary rocks (sandstones and limestones), in metamorphic crystalline rocks (schists and gneisses), and in igneous rocks. Well-known examples of each of these occurrences of the mineral in the southern Appalachian States are described in another part of this paper. Likewise, the occurrence of barite as a replacement of limestone finds ample illustration in Virginia, where it forms an important type of deposit.

Finally, an important mode of occurrence of barite in the known commercial areas of the United States is as a residual mineral, forming masses of varying sizes and shapes in the clays derived by weathering from the decay of limestones. A large part of the barite mined in the Appalachian States and in Missouri is taken from the residual mode of occurrence of the mineral.

CHARACTER OF ASSOCIATED ROCKS.

From the mode of occurrence of barite discussed above, the mineral shows wide range as to kind of rock in which it is found. The numerous occurrences of barite in the Appalachian States afford ample illustration of the wide range in the kind of rock with which it is associated. These include rocks of each of the three major groups—sedimentary, igneous, and metamorphic—and workable concentrations of the mineral are known in each of the three rock groups. Of these, limestones and their residual clays among the sedimentary rocks are vastly the most important sources of supply of the mineral.

Of the sedimentary rocks, limestones and sandstones or their residual clays, especially limestone, are the usual ones which yield workable deposits of the mineral. In at least one locality, however, Prince William County, Virginia, barite is associated with the Triassic red shales and impure limestones as veins. Occurrences of barite in limestone or its residual clays are noted in each of the larger physiographic divisions of the Appalachian States.

The known deposits of barite in igneous and metamorphic siliceous crystalline rocks in the Appalachian region are limited to the Piedmont Plateau, where the mineral occurs as veins, chiefly in schists and crystalline limestones, and occasionally in granite. Examples are known in Virginia, North Carolina, and South Carolina.

ASSOCIATED MINERALS.

These will vary for the individual deposit, but the more commonly occurring ones are found to be dependent in large measure upon the mode of occurrence of the barite. In the vein and replacement types of deposits[4] barite is often associated with metallic sulphides, especially galena, sometimes sphalerite, chalcopyrite, and pyrite; and several of these may be developed in the same deposit. When in quantity, galena is harmful, since it renders the ground product too dark. Quartz, fluorite, and calcite are frequent accompaniments of barite in the deposits of some districts. Fluorite is especially noted in the Kentucky and Tennessee vein occurrences of barite, and in some of the Valley occurrences in Virginia.

In the residual occurrences of barite, the associated minerals will naturally vary with the character of the original rock, but probably the most frequently occurring ones, exclusive of the clay through which the nodular barite is scattered, are the oxides of iron and manganese, and silica in the form of both quartz and chert. In addition to these, tremolite and biotite are noted in some of the Virginia occurrences of barite in the crystalline rocks.

OCCURRENCE AND INDUSTRY BY STATES.

In the following pages the barite industry in the Appalachian States is summarized by states. The treatment is by alphabetical arrangement of the states regardless of their rank as producers.

Alabama.—The known barite deposits in Alabama are confined to the following five counties of the Paleozoic area in the central and northeastern parts of the state: Bibb, Calhoun, Etowah, St. Clair, and Shelby. The most important localities include (1) Maguire Shoals on Little Cahaba River, at the "Sinks" on Six Mile Creek, and near Pratt's Ferry in Bibb County; (2) near Tampa in Calhoun County; and (3) near Greensport in St. Clair County. Barite also occurs at other places in these counties, and is reported from two localities in Shelby County, but these appear to be of doubtful commercial value.[5]

The Alabama deposits of barite are residual in type, probably concentrated in the clay from veins and replacements in the Cambrian and Ordovician limestones, as the early literature contains references to vein occurrences of the mineral. The mineral occurs in loose pieces on the surface, and in lumps, nodules, and irregular masses imbedded in the residual clays derived from the Knox dolomite of Cambrian and Ordovician age, and the Pelham or Trenton (Chickamauga) limestone of Ordovician age. The deposits seem to be localized along lines of folding and faulting, the more important ones being found near the contact of the Knox dolomite with the Pelham or Trenton limestone, although some of the smaller deposits occur entirely within the limits of the residual clays of the Knox dolomite.

In some of the earlier reports of the State Survey, Dr. Eugene A. Smith, State Geologist, refers to many occurrences of barite in veins. Concerning the occurrence of barite in Bibb County, Smith says:[6] "Barite, or heavy spar, is of frequent occurrence in the Quebec

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[2] Lindgren, W.: Mineral Deposits, pp. 98 to 102 (1913). References to the literature cited.

Clarke, F. W.: Bulletin No. 491, U. S. Geological Survey, pp. 553 to 555 (1911). References cited.

[3] Emmons, W. H.: Economic Geology, vol. iii, No. 7, p. 618 (Oct.-Nov., 1908).

[4] No account is here taken of the veins of metallic ores in which barite occurs as a gangue mineral, nor of the occurrences of ore deposits in which barite is developed as a subordinate mineral.

(Knox) dolomite. Maguire's Shoal on the Little Cahaba, and the 'Sinks' on Six Mile Creek, may be mentioned as localities, but barite is found in veins, in many other places." Again, the same author says of barite in Shelby County:[7] "Just south of Calera, and associated with beds of limestone of this group (Chazy and Trenton), is a small bed of limonite exposed in the dry channel of a little branch. The limonite has very intimately mixed with it, in varying proportions, *barite* or *heavy spar*. Some portions of the bed showed almost pure limonite, others limonite and barite in equal proportions, and still others, almost pure barite. Scarcely a hand specimen could be obtained without both minerals.

"Barite in veins constantly accompanies the belt of Chazy limestone described above."

In Berney's *Handbook of Alabama*,[8] Smith states that barite is found in veins in many localities in the Knox dolomite.

The mineral is generally of good quality, usually very pure and white, sometimes grayish and bluish in color, and stained with iron oxide. In some cases the barite is associated with or occurs near limonite deposits, and at times carries more or less galena. Notwithstanding the good quality of the barite in most of the important localities, developments have thus far been slight, and so far as known little or none of the mineral has been placed upon the market. There has been no production of barite in Alabama since 1906. Probably the chief cause for the lack of development of some of the better deposits of the mineral is to be attributed to the absence of a plant in the state to consume the output. The distance and hence freight rates to barite mills in adjoining states are prohibitive for the Alabama product because of a nearer and cheaper source of supply of the mineral.

Georgia.—Barite has been mined at Elton, Murray County, and in the Cartersville district, Bartow County, in northwest Georgia. For some years, however, the entire production has come from the Cartersville district where iron ore, ocher, and barite are mined.

The Elton deposit in Murray County has not been worked in recent years. The composition[9] of the barite from this locality is: $BaSO_4$, 98.82; Al_2O_3, 0.2; Fe_2O_3, 0.33; SiO_2, 0.27; moisture, 0.38 per cent. The mineral is reported to be lower in iron than that mined in the Cartersville district.

The Cartersville district, occupying the southeastern half of Bartow county, includes about 70 square miles, nearly equally divided between the Paleozoic formations (quartzite, limestone, shale, and dolomite) on the west and the older crystalline and metamorphic rocks (schists, gneisses, slates, and conglomerates) of the Piedmont Plain and Appalachian Mountains on the east.[10]

The barite deposits are associated with certain of the Paleozoic formations which occupy the west half of the district, and which named in descending order are: (1) Knox dolomite, (2) Conasauga and Rome formations, (3) Beaver limestone, and (4) Weisner quartzite.

Except the Knox dolomite, these formations belong to the middle or lower Cambrian, and it is probable that the lower portion of the Knox should be classed with the Cambrian. The barite deposits are associated chiefly with the Weisner quartzite and Beaver limestone, though some have been found with the Knox dolomite.

The Weisner quartzite, the basal member of the Cambrian, forms a nearly continuous belt about 19 miles long with an average width of from 1 to 2 miles. It has an estimated thickness of 2,000 to 3,000 ft., and consists of fine-grained quartzite, some beds of fine conglomerate, and interbedded siliceous shale. The conglomerate beds frequently show angular fragments of feldspar, indicating that a part of the material composing it was derived from the granite area to the east. The formation has been intensely folded, and is probably cut by numerous faults, as evidenced by its crushed and brecciated condition in many places. So extensive is the crushing and brecciation in some of the larger mine openings in the district that the original bedding of the quartzite is entirely obscured. The resulting structural conditions of the quartzite have been particularly favorable to chemical action and are responsible for the deposition of the mineral deposits, especially ocher and barite, contained in it.

A chemical analysis made by the N. P. Pratt laboratory on specimens collected by the senior writer from different exposures of the formation gave 4.46 per cent of barium sulphate.

Stratigraphically above, but topographically below the Weisner quartzite, is a thickness of 800 to 1,200

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[5] Smith, E. A., and McCalley, H.: Index to the Mineral Resources of Alabama, Geological Survey of Alabama, pp. 62, 63 (1904).

Grasty, J. S.: Barite Deposits of Alabama, The Tradesman, pp. 35, 36 (July 17, 1913).

[6] Smith, E. A.: Report of Progress for 1875, Geological Survey of Alabama, p. 95 (1876).

[7] Idem, p. 118.

[8] Berney, Saffold: Handbook of Alabama: A complete Index to the State, with a geological map, etc., p. 156 (Mobile, Ala., 1878).

[9] The Mineral Industry, vol. xix, p. 69 (1910).

[10] For a description of the geology and ore deposits of the Cartersville district, see:

Spencer, J. W.: The Paleozoic Group, Geological Survey of Georgia, pp. 99 to 107 (1893).

Hayes, C. W.: Geological Relations of the Iron-Ore Deposits in the Cartersville District, Georgia, Trans., xxx, 403 to 419 (1900).

Hayes, C. W., and Phalen, W. C.: A Commercial Occurrence of Barite near Cartersville, Ga., Bulletin No. 340, U. S. Geological Survey, pp. 458 to 462 (1908).

McCallie, S. W.: A Preliminary Report on a Part of the Iron Ores of Georgia, Bulletin No. 10-A, Geological Survey of Georgia, pp. 109 to 176 (1900).

Watson, Thomas L.: Geological Relations of the Manganese-Ore Deposits of Georgia, Trans., xxxiv, 207 to 253 (1903).

——— A Preliminary Report on the Manganese Deposits of Georgia, Bulletin No. 14, Geological Survey of Georgia, pp. 32 to 99 (1908).

——— The Yellow Ocher Deposits of the Cartersville District, Bartow County, Georgia, Trans., xxxiv, 643 to 666 (1903).

——— A Preliminary Report on the Ocher Deposits of Georgia, Bulletin No. 13, Geological Survey of Georgia (1906). 81 pp.

Maynard, T P.: A Report on the Limestones and Cement Materials of North Georgia, Bulletin No. 27, Geological Survey of Georgia (1912). 293 pp.

Watson, T. L., and Grasty, J. S.: The Geology and Barite Deposits of the Cartersville, Georgia, District, The Tradesman, May 22, 1913, pp. 35 to 37.

ft. of a gray crystalline magnesian limestone, which is shaly in places and at times chert-bearing, known as the Beaver limestone. This limestone forms a narrow belt of lowland along the western margin of and parallel to the ridges of the harder Weisner quartzite. Outcrops of the limestone are seldom seen and its surface is covered by a deep mantle of residual red clay by which the formation may be readily traced.

Barite has two modes of occurrence in the Cartersville district: (1) As deposits from solution in fractures and cavities in the Weisner quartzite in intimate association with the deposits of yellow ocher, and (2) as crystalline nodules and masses of varying size imbedded in the residual clays derived from the decay of the Weisner quartzite and Beaver limestone. Each of these has proved to be a source of supply of barite, but the principal commercial source of the mineral has been from the residual clays. In addition to yellow ocher, the barite deposits of the Cartersville district are more or less closely associated with iron ore.

Barite is found in nearly all the ocher deposits of the Cartersville district. It is known to the miners as the "flowers of ocher," and since it remains in the residual soils derived from the quartzite, it affords the best means of tracing the ocher deposits. It has been shown by Hayes, and later confirmed by Watson, that the ocher deposits with which barite is associated are the direct replacements of the silica in the Weisner quartzite from thermal solutions circulating along the zones of fracture. These relations are best indicated at the mine of the Georgia Peruvian Ocher Co., at the wooden bridge over Etowah River. Here large clusters and groups of magnificent barite crystals are found in the pockets of ocher and in the fractures and cavities of the quartzite. The usual occurrence of barite is in divergent groups of massive tabular crystals, giving a crested appearance and grading into both straight and curved laminated masses. Groups of crystals weighing 25 lbs. and more are not uncommon. It seems probable as Hayes states, that the crystals of barite "were probably deposited after the conditions favorable for the solution of silica and the deposition of ocher had passed. Groups of acicular crystals of this mineral, several inches in length, are not uncommon. It also occurs in white granular veins."[11]

A second and commercially more important occurrence of barite in the Cartersville district is as nodules and masses of varying sizes and shapes imbedded in the residual clays. Deposits of this type of the mineral are rather widely distributed over the district, but probably many of them will not prove profitable because of lack of sufficient concentration for mining alone. However, a number of promising deposits have been opened, but further development is necessary before a definite statement can be made as to the extent, quality, and workability of the deposits in the district.

The principal barite deposits occur near the south end of the quartzite belt where the structure has been shown to be anitclinal. The deposits are found on the east side of the anticline lower down the slope but adjacent to a belt of limonite which rests directly on the quartzite and has been mined for many years. According to Hayes and Phalen,[12] "while this belt has not been sufficiently prospected to prove the continuity of the deposits, their thickness is indicated by a tunnel which has been driven into the side of the hill about 300 ft. north of the present workings. This tunnel penetrates 120 ft. of the barite-bearing clay and then enters the iron ore." (See Fig. 2).

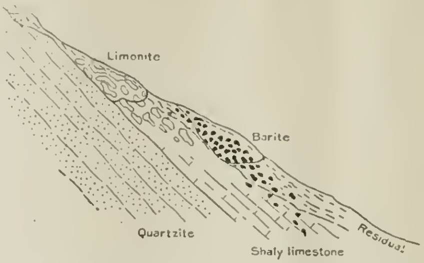

Fig. 2. Sketch Showing Relations of Barite and Limonite to Underlying Formation Near Carterville, Ga.

Concerning the relations of the limonite and barite to the underlying formations Hayes and Phalen say:[13] "One striking feature is the sharp separation between the two minerals; each appears to occupy a definite horizon, and so far as observed there is no intermingling. While both in their present condition are residual, they appear originally to have replaced distinct beds in the shaly limestone overlying the quartzite, the iron being deposited immediately adjacent to the quartzite, and the barite, for the most part, at least, in higher beds. It is highly probable that deposition of the barite and limonite took place, in part, at least, simultaneously. It is quite certain that gravity has been largely instrumental in concentrating the former into a workable deposit."

The barite deposit is described as having a thickness of 50 ft. normal to the surface slope; is intermingled with residual clays containing fragments of quartzite; and the barite makes up about a third of the material mined. The barite forms nodules weighing several ounces up to boulders of several hundred pounds; is mostly massive and compact granular in texture; and of pure white to bluish color.

Kentucky[14]—Barite is reported to have been first marketed from Kentucky in 1903, when shipments were made from western Kentucky and from Scott County in central Kentucky. With the exception of a small tonnage in 1907 from western Kentucky, the production has been from the central part of the state.

In Kentucky barite deposits are known in (1) the central and (2) the western parts of the state. Thus far mining of barite in the state has been confined chiefly to the central or Blue Grass region, which comprises the following 16 counties: Anderson, Bourbon, Boyle, Clark, Fayette, Franklin, Garrard, Harrison, Henry, Jessamine, Lincoln, Madison, Mercer, Owen, Scott, and Woodford. Of these, Boyle, Fayette, and Garrard counties, in the order named, are the principal producers of barite. The map, Fig. 3, shows the location of the principal barite deposits in the central Kentucky region.

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[11] Hayes, C. W.: Trans., xxx, 418 (1900).

[12] Hayes, C. W., and Phalen, W. C.: Bulletin No. 340, U. S. Geological Survey, p 461 (1908).

[13] Idem, p. 461.

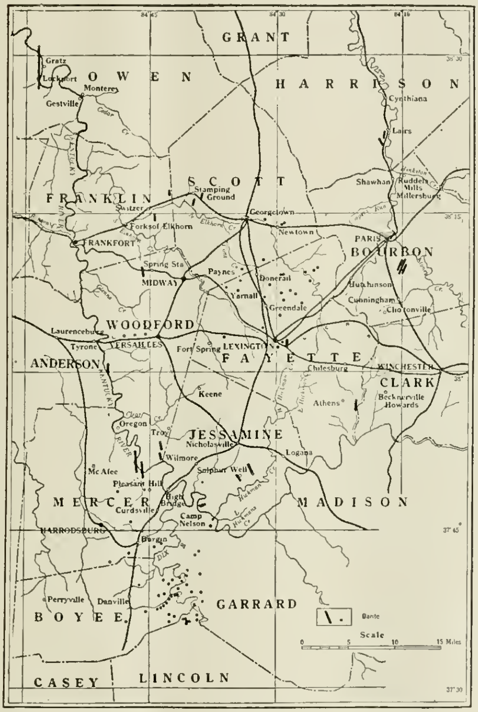

Fig. 3. Principal Barite Deposits in Central Kentucky.

The barite deposits of central Kentucky are confined to the Ordovician and are most prominently developed in the lower or Mohawkian division of the Ordovician, more especially in the limestones of Stones River and Trenton age and in the Eden shale. The rocks are all sedimentary and the important deposits of barite are confined to the limestone members. The barite occurs chiefly in veins filling simple fissures or faults, chiefly the latter. The veins are vertical or slightly inclined. They vary in width up to 24 ft., but the usual width is from 1 to 3 ft. The thickness of individual veins varies much from point to point, swelling or pinching both laterally and vertically. They are apt to become lean and barren in the argillaceous beds, but are of good grade in the limestone beds. According to Miller, the veins seem to have considerable vertical extent, and mining operations on some of them have extended to depths ranging from 100 to 325 ft., without noticeable tendency to close up.[15]

The barite deposits of central Kentucky are either of the fissure, breccia, or replacement type, or a combination of these. The breccia deposits are associated with faults. The principal minerals associated with the barite are calcite, fluorspar, sphalerite, and galena, with quartz, marcasite, pyrite, chalcopyrite, smithsonite, limonite, and manganese oxide less frequent. Strontianite and celestite are reported to occur (see analyses below).

The following analyses[16] (Table I) of barite from the central Kentucky region are of interest.

Attention is especially directed to the large but variable amount of strontium oxide reported in most of the analyses.

In the western Kentucky region barite is found in the following eight counties: Caldwell, Christian, Crittenden, Cumberland, Livingston, Lyon, Russell, and Trigg, but the most important deposits are confined to three of these, namely, Caldwell, Crittenden, and Livingston. This area forms the well-known fluorspar district of western Kentucky, and thus far the barite deposits are incidental to those of fluorspar, just as fluorspar is incidental to the barite deposits of central Kentucky. Most of the deposits have been worked for fluorite and the sulphides, since barite is not particularly abundant. According to Fohs, the most important deposits of barite in the western Kentucky region are: "Commercial shaft, Meyers, Sullenger, and Bibb in Crittenden County; the Lindley, Stone, and Bradshaw in Livingston County; and the Satterfield, Ray, and Lowery in Caldwell County."

The barite of western Kentucky is found chiefly as a vein mineral in the fluorspar deposits, which, according to Smith, occur as (1) vein deposits filling fissures due to faulting; (2) ores cementing breccias; and (3) metasomatic replacements. The vein deposits (fluorite, barite, some galena, and some sphalerite) filling faults are by far the most important occurrence. The faults strike northeast, northwest, and east, though a few unimportant ones have a northerly direction. The veins occur in the formations of the Chester and Meramec groups, especially in Ste. Genevieve and St. Louis limestone, of Carboniferous (Mississippian) age. In Crittenden County vertical dikes and horizon-

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[14] Fohs, F. Julius: Barytes Deposits of Kentucky, Kentucky Geological Survey, ser. iv, vol. i, pt. 1, pp. 441 to 588 (1913).

Grasty, J. S.: Barite Deposits of Kentucky, "The Tradesman," July 3, 1913, pp. 33, 34.

Miller, A. M.: The Lead and Zinc Bearing Rocks of Central Kentucky with Notes on the Mineral Veins, Bulletin No. 2, Kentucky Geological Survey (1905), 35 pp.

Ulrich, E. O., and Smith, W. S. T.: Lead, Zinc and Fluorspar Deposits of Western Kentucky, Bulletin No. 213, U. S. Geological Survey, pp. 205 to 213 (1903).

——— The Lead, Zinc and Fluorspar Deposits of Western Kentucky, Professional Paper No. 36, U. S. Geological Survey (1905), 218 pp.

The Barite Deposits of Western Kentucky and Union County will be described in Bulletin No. 15, to be issued shortly by the State Geological Survey.

[15] According to Fohs, the veins "may reach a depth of over 1,200 ft., a length of four or five miles and a width of 16 ft. The average present depth of the known deposits is 600 ft., at least half of which carries a commercial product."

[16] Fohs, F. Julius: Kentucky Geological Survey, ser. iv, vol. i, pt. 1, pp. 449 to 451 (1913).

tal sheets of peridotite occur ranging up to 25 ft. in width. The veins dip at a high angle, usually 60° or more, and are subject to change both in dip and strike. They show considerable variations in width, but the most important ones do not exceed 6 or 8 ft., and many of them are reported to pinch out completely for short distances. Besides angular fragments of the country rock, the veins are composed of the minerals fluorite, calcite, barite, sphalerite, and galena, occasionally quartz and pyrite, and rarely others. Banding is a pronounced structural feature.

Concerning the occurrence of barite, Smith says:[17]

> Barite is common in some of the veins, although in many if not most of them it is not found at all. Taking the district as a whole, however, it is probably next in abundance to calcite as a vein mineral. In many cases where it occurs it forms only a small proportion of the vein, although occasionally it is the chief constituent, as at the Lowery mine, at one of the Myers prospects, and at the Bateman prospect. Seams in brecciated rocks and narrow veins sometimes consist wholly of this mineral.
>
> Barite occurs in all of the rocks in which fluorite is found —in Chester quartzite and in both Ste. Genevieve and St. Louis limestone. Where seen only in small amounts it was, as a rule, along the margin of the vein and never distributed through it. When occurring with fluorite in seams, it sometimes shows symmetrical banding.
>
> The only vein of this mineral which has been developed to any extent is that on which the Ray and Lowery shafts are situated. Here the vein has a width of several feet near the surface, pinching to from 6 inches to a foot at a depth of 30 or 35 feet. It consists almost entirely of barite, with a very small proportion of fluorite and calcite. It is more or less banded, and locally one of the central bands, from a fraction of an inch to 2 inches in width, contains a considerable amount of medium-grained sphalerite.

The various writers who have studied the western Kentucky vein deposits are generally agreed that they were formed from solution, and that the source of the minerals has been from the limestones of the region. It is not impossible that the source of some of the minerals at least may have been the magma from which the peridotite dikes were derived. Smith says:[13] "It is not probable, however, that the dikes themselves are the source of the fluorite, chiefly on account of the total volume of the fluorite veins as compared with that of the igneous dikes and the very small fluorine content of the peridotite."

Maryland—In Maryland barite occurs in Frederick and Carroll counties, and small occurrences have been reported in the Hagerstown Valley which are similar to those found to the northeast in Pennsylvania. However, the deposits in Frederick and Carroll counties give the greater promise of eventually becoming of economic importance. The deposit here described may, broadly speaking, be considered as typical. Its association with the Piedmont limestones suggests that further search for barite in this particular physiographic province (Piedmont) would be worth while. Deposits similar to that on the Sauble property occur not only in the Piedmont limestones of Virginia but are also found at the same geologic horizon in North Carolina and South Carolina.

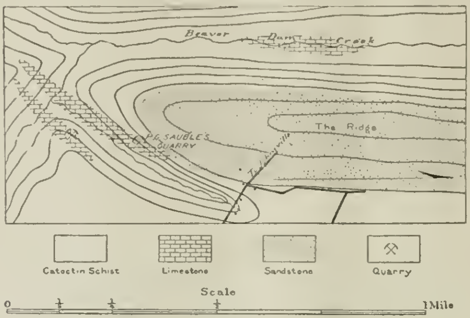

Fig. 4. Map of Sauble Quarry and Vicinity Near Union Bridge, Md.

The Sauble property is located on a small feeder of Beaver Dam Creek in Frederick County and to the east of the large quartzite ridge extending in a northeast-and-southwest direction between Johnsville and Union Bridge. Structurally, the rocks of this ridge appear to be compressed into a syncline overturned to the westward. The quartzite is tentatively correlated

TABLE I.—ANALYSES OF KENTUCKY BARITE.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Ignition	0.17	0.34	0.87	0.28	0.62	0.23	1.40	0.65	0.15	1.19	0.28
SiO_2	0.34	0.11	0.11	0.25	0.10	0.05	0.55	0.18	0.10	0.20	0.23
Fe_2O_3	0.06	0.02	0.04	0.06	0.06	0.03	0.06	Trace	0.04	0.08	Trace
BaO	50.86	50.96	60.26	64.72	59.80	50.96	54.95	10.71	64.68	49.98	60.55
SrO	8.99	11.65	3.80	Trace	2.41	11.10	6.75	45.06	0.20	11.07	3.72
CaO	3.61	Trace	0.76	Trace	2.09	0.88	0.20	0.25	Trace	Trace	Trace
SO_3	33.87	36.31	34.60	33.82	33.23	35.66	34.22	42.28	33.97	35.12	35.38
F	2.45	Trace	0.52	0.00	1.42	0.60	0.14	0.00	0.00	0.50	0.00
ZnO	Trace	0.00	0.00	0.00	0.00	0.00	1.23	0.00	0.00	1.50	0.00
Total	100.35	99.39	100.96	99.13	99.73	99.51	99.50	99.13	99.14	99.68	100.16

I. John Baughman prospect, one-half mile north of Danville, Boyle County.
II. Lee River prospect, one-half mile south of Harrodsburg, Mercer County.
III. Farris prospect, 4 miles northeast of Danville, Boyle County.
IV. Meyers prospect, near Mexico, Crittenden County.
V. Ray mine, 2 miles from Fredonia, Caldwell County.
VI. Ray mine, 2 miles from Fredonia, Caldwell County.
VII. Hayden open cut, 1½ miles south of Danville, Boyle County.
VIII. Celestite from Truesdale, Owen County.
IX. Perkins prospect, 1½ miles southeast of Burgin, Mercer County.
X. Mosby prospect, 1½ miles south of Shryock Ferry, Woodford County.
XI. Shelton open cut, 4 miles east of Danville, Boyle County.

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[17] Professional Paper No. 36, U. S. Geological Survey, p. 135 (1905).

with the Weverton formation and is underlain by the Loudon, which is composed here of limestone and shale. (Figs. 4 and 5).

The barite on the Sauble property occurs in the shape of small bands, stringers, etc., in the Loudon limestone, which, as would be inferred from the structural relations referred to above, is greatly fractured and crushed, and in the overlying shale fracturing and crushing are even more emphasized. The quarry opened here has never been worked, however, for barite, but was operated with a view to obtaining limestone for calcination for local use, with no attention given to the barite. Judging from the lumps and small piles of barite lying about, it would seem that, to some extent at least, the mineral was sorted out and thrown aside.

Barite is also found at other localities in the Piedmont province of Maryland, and is characterized by occurring in crushed zones and along lines of dislocation which resulted from movements that profundly compressed and more or less altered all the rocks of the region. These limestones were formerly much more widely distributed, but, in general, only the portions which have been compressed and preserved by reason of their synclinal structure now remain, and in most instances they have been greatly crushed and fissured and recemented by calcite, and here and there by barite.

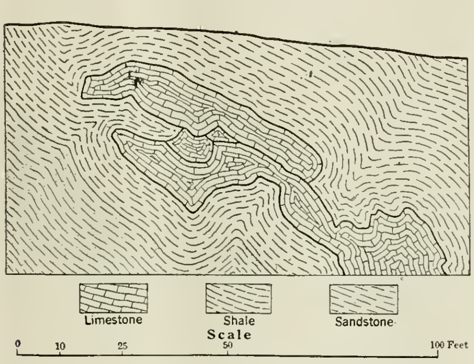

Fig. 5. Section of Sauble Quarry, Maryland.

North Carolina[19]—North Carolina is one of the important barite producing states in the Appalachian region. Deposits of barite occur in Gaston and Orange counties in the Piedmont region, and in Madison County in the western part or mountainous region of the state, but the production is confined to Gaston and Madison counties.

In Orange County, barite of good quality is found about 3.5 miles southeast of Hillsboro, near the Chapel Hill road. Some development work was carried on in 1901.

Barite is found at several localities in the vicinity of King's and Crowder's mountains, but the principal producing mine is located about 5 miles south of Bessemer City, Gaston County, near the north end of Crowder's Mountain. The barite occurs in quartz-sericite schist, as veins ranging in thickness from 2½ to 6 ft. as exposed in the workings. The veins strike about N. 10° to 15° E., and dip at high angles, usually toward the west; in some places they are nearly vertical. Mining of barite has been carried on at a number of places in the vicinity of the Lawton mine, as shown in many old workings. Cyanite schist outcrops near the veins on the west side and lenses of magnesian limestone occur in the region, but so far as observed are not found in association with the barite.

The barite is granular, sometimes coarsely crystalline, and in places cleavage surfaces 2 ins. across are noted. The associated minerals are quartz, galena, sphalerite, pyromorphite, and stains of iron and manganese oxides. According to Pratt, the veins are lenticular in shape, and probably represent the filling of fissures and crevices in the schists, which may have been caused by the faulting or tearing apart of the rock.

In Madison County in western North Carolina, the barite deposits occupy an area about 5 miles long extending a little north of east from Bluff on Spring Creek to and across French Broad River. Within this area barite has been worked chiefly in the vicinity of Marshall, Stackhouse, Sandy Bottom, and Hot Springs. According to Keith, the barite occurs as irregular veins in pre-Cambrian granites and to a less extent in Cambrian feldspathic quartzite. Watkins[20] reports that some of the deposits are associated with limestone. Pratt states that the veins vary from 3 to 10 ft. in thickness and the barite is practically free from other minerals. At the Stackhouse mine Pratt reports that outcroppings of barite have been observed on the surface for a distance of 2,200 ft. The map, Fig. 6, gives a good general idea of the geology of the barite area in western North Carolina.

Keith gives the following description of the deposits:[21]

> The country rock was much broken and shattered before the formation of the barite, and the spaces were filled with the ore. From the arrangement and crystalline condition of the barite, it is evident that it was deposited from aqueous solutions. As to the derivation of the material in solution there is no evidence; probably it came from the great mass of granite within which it is now found. All of these barite areas occur in a belt near and parallel to one of the principal thrust faults of the region. The rocks were greatly disturbed during the production of the original fault plane, and later, to a less extent, during its secondary deformation. It appears most likely that the crushing of the quartzites seen in the barite deposits was associated with this later deformation. In the old workings on Spring Creek, near the level of the creek, the barite-bearing quartzites are very close to the thrust fault and there seems to be a distinct connection between the fault and the barite. The barite occurs in large crystals and crystalline masses which have not been

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[18] Idem, p. 151.

[19] Keith, Arthur: Asheville Folio, North Carolina-Tennessee, No. 116, U. S. Geological Survey, p. 9 (1904).
Pratt, J. H.: Economic Paper No. 6, North Carolina Geological Survey, p. 62 to 65 (1902).

[20] Personal communication, October, 1914.

deformed, as were the minerals of the inclosing rocks. From this it is clear that the barite was deposited after the period of faulting and folding, and although the shattering of the rock may have been due to the folding, the barite must have been introduced later. The crevices in the shattered granite afforded comparatively easy access to the solutions that carried the barite, but no direct connection in origin can be traced between the faults and the barite deposits.

At present only the deposits on Spring Creek are being mined. A considerable amount of barite was taken from the veins a mile southeast of Stackhouse, but the deposits on Doe Branch were never developed to any extent. Southeast of Stackhouse small open cuts were made and short shafts and tunnels were driven. These were nearly on the crest of a ridge, and penetrated for some distance the more or less weathered granites. On Spring Creek the mining has been done chiefly through open cuts. These are now of considerable size and much material has been removed. The openings lie on ridges which are about 500 ft. above water level and which slope steeply toward Spring Creek. The surroundings are thus favorable for extensive operations, and the quantity of barite appears to be large.

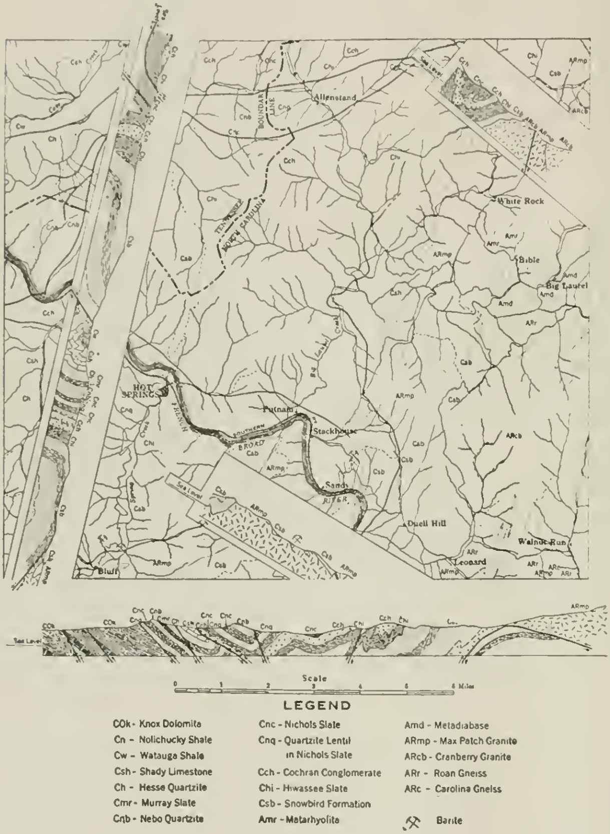

Fig. 6. Map and Sections of Barite Area in Western North Carolina.

Pennsylvania[22]—Barite is not mined on a commercial scale in Pennsylvania at present, although small shipments have been made from the Cumberland Valley in the southern part of the state in the vicinity of Waynesboro, Franklin County. Barite is also reported from west of New Hope, Butler County; at Phœnixville mines, and in small quantity in old Jug Hollow mine, Schuylkill township, Chester County; formerly mined at Fort Littleton, Fulton County; and at the Perkiomen copper mines, Montgomery County.

In the vicinity of Waynesboro the barite is associated with Cambrian limestones and their residual clays. Openings have been made to the north, east, and northeast of Waynesboro both in the residual clays and in the limestone. The deposits are found in the folded and brecciated portions of the limestone, and the barite occurs in the brecciated rock as a vein filling, but such deposits are not considered profitable. Stose says of the barite in the two openings made in bedrock (limestone) visited by him: "Here the barite is chiefly massive, banded, sub-crystalline or granular, and milky, resembling chert, but is in part clear and crystalline." In the residual deposits the lumps or masses of barite average 6 to 8 in. in diameter, are rough in outline with evidence of dissolved limestone fragments, and are considerably weathered.

South Carolina[23]—The known commercial deposits of barite in South Carolina are confined to Cherokee County on the North Carolina line. The production has been small and irregular, not, however, on account of lack of quantity and quality of the mineral. The deposits are located in the vicinity of Kings Creek, a station on the Blacksburg-Yorkville branch of the Southern Railway, and are about 13 miles southwest of the Lawton mine in Gaston County, North Carolina.

The barite occurs in quartz-sericite schist as lenticular veins. Thus far limestone has not been observed in association with the barite deposits. The development work done comprises open cuts and pits, which expose in places as many as three parallel veins ranging from 1 to 3 ft. in thickness. Watkins reports the greatest thickness observed was more than 6 ft. of massive white barite exposed in an open cut north of the railroad. The veins have a general strike of about N. 25° E., and dip about 40° to 45° southeast. On the property of the Cherokee Chemical Co., the veins east of the railroad dip to the southeast while those on the

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[21] Keith, Arthur: Asheville Folio, North Carolina-Tennessee, No. 116, U. S. Geological Survey, p. 9 (1904).

[22] Stose, G. W.: Bulletin No. 225, U. S. Geological Survey, pp. 515, 516 (1904).

Sanford, S., and Stone, R. W.: Useful Minerals of the United States, Bulletin No. 585, U. S. Geological Survey, p. 158 (1914).

west side dip to the northwest, indicating erosion of an anticlinal fold. They conform roughly to the structure of the inclosing schists, and sharp contacts between vein and country rock are usually shown, though small inclusions of the schist are incorporated in the barite in places. Discordance of strike is noted in places, as the veins cut the schists at a slight angle. Branching veinlets are given off from the main veins which fill fractures that cross the structure of the schists. The field evidence indicates that the veins have had a similar genesis to those farther northeast in Gaston County, North Carolina.

The barite is of good quality, massive granular in structure, and varies from pure white to pink in color, the white predominating. The pink is mixed with the white barite in milling, since there is apparently no difference in quality of the two differently colored materials. Some parts of the veins are very pure, being singularly free from associated minerals, but other parts contain a little galena and less fine-grained quartz. Sloan states that occasional inclusions of pyrite cause local areas of stain. The barite is generally of good bleaching quality.

The mill of the Cherokee Chemical Co. is located directly alongside the railroad track and the deposits have been opened at a number of points both to the north and south of the mill, with most of them lying within a radius of half a mile therefrom. The following analysis by Rickets & Banks of a representative sample of the white barite collected by Banks from the property of the Cherokee Chemical Co., located at Kings Creek, indicates its composition: $BaSO_4$, 93.59; Fe_2O_4, 0.32; CaO, 0.02 per cent; MgO, trace; SiO_2, 4.76 per cent.

(To be concluded.)

RADIUM, URANIUM, AND VANADIUM IN 1914.

The year 1914 was an eventful one in the industry of mining radium, uranium, and vanadium ores and had by far the largest year's production yet made. Figures collected by Frank L. Hess, of the United States Geological Survey, indicate that the output amounted to about 4,300 short tons of dry ore carrying 87 tons of uranium oxide and 22.4 grams of metallic radium. The ore was valued at about $445,000. The ore produced in 1913 contained 41 tons of uranium oxide and 10.5 grams of radium, and that produced in 1912 contained 26 tons of uranium oxide and 6.7 grams of radium. About nine-tenths of the contained radium is thought to be recoverable under improved processes.

Although carnotite, a mineral of these rare metals, contains three times as much uranium oxide as vanadium oxide, the Colorado and Utah ores of these metals generally contain other vanadium minerals in such quantity that vanadium oxide is present in excess of the uranium oxide. However, little is paid for the vanadium, as its separation from uranium is troublesome, and only a few thousand dollars was received in 1914 by brokers or producers for the vanadium in the ores sold. Sandstone impregnated with roscoelite, a vanadium-bearing mica, is mined at Vanadium, San Miguel County, Colo., on the eastern edge of the carnotite field, by the Primos Chemical Co. The total quantity of vanadium in the carnotite and other ores mined during the year was apparently about 432 tons.

About the beginning of 1914, owing to the very high prices charged for radium salts, their scarcity, their evident usefulness in treating cancer and other hitherto incurable diseases, the practical impossibility of the poor receiving treatment by radium because of its scarcity and high cost, and to the fact that much of the radium-bearing ore was being shipped out of the country, Secretary of the Interior Lane caused to be introduced in Congress bills reserving radium-bearing lands from entry as mining claims, and providing for government purchase. The bills are still pending.

During the year the National Radium Institute conducted, under the supervision of the Bureau of Mines, mining operations at Long Park, near Paradox Valley, in Montrose County, Colo., and a plant at Denver for the production of radium and investigation of processes. The work has been so encouraging that Director Holmes has announced the probable production of radium at one-third of its present cost. Messrs. Lind and Whittemore, of the Bureau of Mines, state that their investigations show that carnotite carries proportionally to its content of uranium as much radium as pitch-blende or other uranium minerals—that is, the radium has reached its maximum ratio to the uranium from which it is derived and is thus in equilibrium. From published results of experiments made on casual specimens of carnotite it had been popularly supposed that carnotite was less rich than pitchblende in radium.

In Utah the Standard Chemical Co. made the first commercial production of carnotite ores from the Henry Mountains during the year, and the commercial production of uvanite, a radium-bearing mineral new to science, accompanied by other uranium minerals, one or more of which are yet to be described, was begun at Temple Rock, 45 miles southwest of Green River. Shipments were made from newly opened carnotite deposits at Court House, northwest of Moab, Utah, and from deposits 16 or 18 miles southwest of Moab. A first shipment was also made from Blue Mountain, Routt County, Colo.

The Paradox Valley region was, however, as usual the chief producing area, and from it came the bulk of the ores. The Standard Chemical Co. was the largest single producer and shipped more than half of the country's output.

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[23] Sloan, Earle: Catalogue of the Mineral Localities of South Carolina, Bulletin No. 2, ser. iv, South Carolina Geological Survey, pp. 125, 126 (1908).

Unpublished data furnished by Joel H. Watkins, geologist for the Southern Railway Co., Washington, D. C.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Distilled Liquors.

Distilled liquors contain a high alcoholic content and a low extract or residue. When distilled they contain no residue. But by storing in casks the liquors absorb extractives from the wood. These extractives impart also flavor and color.

In pitching a distil mash the object sought is a high ethyl alcoholic yield. When the fermented alcoholic mash is distilled under ordinary working conditions, a distillate results containing a mixture of alcohols and water. Ethyl alcohol is the main constituent while small amounts of the higher boiling alcohols—amyl, butyl, propyl, etc., and their esters, are present and constitute what is known as fusel oil. The product of the distil mash varies in flavor and character with the ingredients used for the basis of the mash.

The fusel oil varies considerably in composition with the source from which it is derived. Amyl alcohol is its chief constituent. The table below gives the alcohols found in fusel oil with their formulas, specific gravity, and boiling points:

	Formula.	Specific Gravity.	Boiling Point.
Ethyl alcohol	C_2H_5OH	0.794	78.4° C.
Propyl alcohol	C_3H_7OH	0.820	97° C.
Butyl alcohol	C_4H_9OH	0.803	115° C.
Amyl alcohol	$C_5H_{11}OH$	0.811	130° C.
Hexyl alcohol	$C_6H_{13}OH$	.....	......

The following acids have been found in fusel oil. They are usually combined with the alcohols to form ethers: Acetic, propionic, butyric, valerianic, caproic œnanthylic, caprylic and Pelargonic.

Whiskey is made from a fermented infusion known as a mash. This mash is made by steeping in water, starch containing material, as barley, rye, corn (maize) or oats mixed with malt. The malt contains the diastase which converts the starch into fermentable sugars—maltose and dextrine. In mashing for whiskey a maximum yield of maltose and a minimum of dextrine is tried for. A yeast is added and alcoholic fermentation allowed to proceed. The fermented wort is then distilled without rectification or separation of the fusel oil and other congeneric substances which are valuable as flavors. The "low wine," the product of the first distillation, is redistilled; the product of the second distillation is usually divided in three fractions, of which the middle portion, called clean spirit, is retained for the whiskey while the first ("foreshots") and the last fractions ("feints") are mixed with the next portion of low wine to be redistilled. When the whiskey is too high in alcohol it is diluted with water to proper strength.

New whiskey is aged by storing in casks for a number of years. The whiskey is colorless when stored, but is colored and flavored from the charred casks in which it is stored. Its flavor varies considerably from the grain used in the mashing.

The following are the standards of the joint committee of the A. O. A. C. and the A. S. N. F. D. D.:

New whiskey is the properly distilled spirit from the properly prepared and properly fermented mash of malted grain, or of grain, the starch of which has been hydrolyzed by malt; it has an alcoholic strength corresponding to the excise laws of the various countries in which it is produced, and contains in 100 liters of proof spirit not less than 100 grams of the various substances other than ethyl alcohol derived from the grain from which it is made, and of those produced during fermentation, the principal part of which consists of higher alcohols estimated as amylic.

Whiskey (potable whiskey) is new whiskey which has been stored in wood not less than four years without any artificial heat save that which may be imparted by warming the storehouse to the usual temperature, and contains in 100 liters of proof spirit not less than 200 grams of the substances found in new whiskey save as they are changed or eliminated by storage, and of those produced as secondary bodies during ageing; and, in addition thereto, the substances extracted from the casks in which it has been stored. It contains when prepared for consumption as permitted by the regulations of the Bureau of Internal Revenue not less than 45% by volume of ethyl alcohol and if no statement is made concerning its alcoholic strength, it contains not less than 50% of ethyl alcohol by volume, as prescribed by law.

Rye whiskey is a whiskey in the manufacture of which rye, either in a malted condition or with sufficient barley or rye malt to hydrolyze the starch, is the only grain used.

Bourbon whiskey is a whiskey made in Kentucky from a mash of Indian corn and rye and barley malt of which Indian corn forms more than 50%.

Corn whiskey is whiskey made from malted Indian corn or of Indian corn the starch of which has been hydrolyzed by barley malt.

Blended whiskey is a mixture of two or more whiskeys.

Scotch whiskey is a whiskey made in Scotland solely from barley malt, in the drying of which peat has been used. It contains in 100 liters of proof spirit not less than 150 grams of the various substances prescribed for whiskey exclusive of those extracted from the cask.

Irish whiskey is whiskey made in Ireland and conforms in the proportions of its various ingredients to Scotch whiskey, save that it may be made of the same materials as prescribed for whiskey and the malt used is not dried over peat.

U. S. P. Standards: Whiskey should be at least two years old; its specific gravity should be between 0.945 and 0.924; its alcoholic content not less than 37% nor more than 47.5% by weight; its residue from 100 c.c. should not be more than 0.5 gm., which should be neither sweet nor spicy, should dissolve in 10 c.c. cold water and this solution should be colored only a pale green when treated with a drop of very dilute ferric chloride solution (a deeper color indicates more than traces of tannin).

The last traces of the liquor volatilized on the water bath should have an agreeable odor free from harshness, indicative of the absence of fusel oil. Its reaction should be slightly acid, but not more than 1.2 c.c. of normal alkali should be required to neutralize 100 c.c. of the liquor, using litmus as an indicator. If 25 gms. of kaolin are shaken vigorously with 50 c.c. of the liquor and allowed to stand an hour, then filtered, the color should not be much lighter than before the treatment.

Whiskey consists chiefly of ethyl alcohol and water, with relatively small amounts of fusel oil, acids, esters, aldehydes, and furfural. Its extract derived mainly from the casks in which it is stored, should consist only of small amounts of tannin, sugar, and coloring matter.

British whiskies: Scotch and Irish whiskies are aged in charred barrels, therefore they are of lighter color than American whiskies. Scotch whiskey has its smoky taste, obtained from the peat over which it is dried.

American whiskies have a deeper color than the British, due to the charred barrel; also a rich fruity flavor without the suggestion of smoke.

In Table I are given the analyses by Shepard of fourteen leading brands of American whiskies. They vary in age from four to eight years. Two samples of neutral spirits used for compounding and adulterating are also given.

The results of an analysis by Crampton and Tolman of rye and bourbon whiskies at different stages of aging appear in Table II. After three or four years, the acids and esters do not materially change while prior to this time there was a marked increase in the actual amounts of all the constituents determined except fusel oil, over and above that due to concentration. There is a larger amount of solids, acids, esters, etc., in rye whisky than in the bourbon. This is due to heated warehouses used in storing the former and unheated in the latter.

Whisky is often adulterated by compounding. Neutral spirits and whisky are mixed and then artificially colored and flavored. This mixture cannot be called a "blend" according to U. S. decisions which restrict "blended whisky" to a mixture of different kinds of genuine whisky, colored and flavored. Imitation whisky is often made by diluting with water neutral spirit or alcohol to the proper strength, adding for flavor some one of certain essential oils, as oil of wintergreen and artificial fruit essences, such as œnanthic and pelargonic ethers (generally also a small amount of pure whisky is added to help flavor) giving the mixture a body by adding prune juice and coloring by the addition of caramel.

TABLE I.

			Grams per 100 Liters								
					Acids						
	Age, Years.	Alcohol per cent by weight.	Extract.	Ash.	Total.	Fixed.	Volatile.	Esters.	Aldehydes.	Furfural.	Fusel Oil.
Rye	8	50.1	189.8	7.7	92.0	12.8	79.2	81.8	17.5	3.0	84.9
Bourbon	8	50.1	181.5	7.3	68.4	9.3	59.1	60.7	17.5	3.2	102.6
Standard	5	50.0	160.4	7.2	66.8	10.2	56.6	55.9	10.0	2.4	160.4
Hand Made Sour Mash	4½	50.8	162.1	7.4	67.1	10.2	56.9	74.8	12.0	2.6	130.9
Hand Made Sour Mash	4	50.2	148.5	7.3	62.4	7.5	54.9	55.9	15.0	2.6	152.0
Hand Made Sour Mash	4	49.9	132.7	5.8	49.2	7.5	41.7	39.6	8.0	1.0	107.4
Hand Made Sour Mash	6	50.4	138.6	6.4	74.8	8.6	66.2	61.6	10.5	1.3	192.7
Hand Made Sour Mash	6	50	153.7	9.7	58.8	9.9	48.9	69.6	14.0	0.7	137.1
Hand Made Sour Mash	7	50	180.0	10.0	74.4	9.9	64.5	70.8	12.5	2.5	117.0
Bourbon	5½	49.9	129.3	5.1	60.9	7.2	53.7	49.3	9.5	0.8	141.7
Special Reserve	7	49.8	212.0	8.0	93.0	13.5	79.5	94.0	22.5	5.0	119.5
Sour Mash	5	50.1	124.5	7.2	58.2	7.2	51.0	64.0	9.5	0.5	95.3
Sour Mash	7½	49.8	177.2	7.3	66.5	9.0	57.5	76.6	10.0	1.7	193.6
Sour Mash	4	50.1	139.4	6.5	50.3	6.3	44.0	54.6	7.5	1.5	152.0
Neutral Spirits		95.6	10.3	0.9	7.5	1.2	6.3	15.4	2.5	...	30.0
Neutral Spirits		94.4	3.2	0.0	6.3	1.4	4.9	64.2	11.0	...	39.6

One of the very lowest grades of blended whisky is made from a recipe of Fleischman's:

Spirits	32 gallons
Water	16 gallons
Caramel	4 ounces
Beading oil	1 ounce

"Beading oil" is prepared by mixing 48 ounces of oil of sweet almonds with 12 ounces of C. P. sulphuric acid, neutralizing with ammonia, adding double the volume of proof spirits and distilling. This preparation is called "beading oil" because it is used for puting an artificial bead on cheap liquors.

The burnt taste peculiar to Scotch whisky is often imitated by adding a little creosote. Sugar is found as a frequent adulterant.

The analysis by Ladd, Table III, shows the composition of neutral spirits and imitation whisky consisting of neutral spirits diluted with water, colored with caramel and flavored.

In a broad sense brandy is the name applied to the product resulting from the liquor distilled from the juices of fruits such as grapes, apples, peaches, cherries, plums, etc. The finest grades of brandy such as pure cognac and armagnac are (by use of pot stills) made in France from the best grades of white wine. The poorer grades of brandy are distilled from cheap wines the residue or pomace of fermented fruits and from the lees and scrapings from the cask.

The best brandies are rectified by a second distillation.

Brandy consists of nearly pure alcohol and water and its flavor is due to the source of the wine it is made from.

TABLE II.—SUMMARY OF ANALYSES OF AMERICAN WHISKIES OF DIFFERENT AGES.

		Grams per 100 Liters of Proof Spirits						
	Proof.	Color.	Extract.	Acids	Esters.	Aldehydes.	Furfural.	Fusel Oil.
Rye Whiskey—								
New—Average	101.2	0.0	13.3	4.4	16.3	5.4	1.0	90.4
Maximum	102.0	0.0	30.0	72.0	21.8	15.0	1.9	161.8
*Minimum	100.0	0.0	5.0	12.0	4.3	0.7	trace	61.8 43.7
One Year Old—Average	102.5	8.8	119.7	46.6	37.0	7.0	1.8	111.5
Maximum	104.0	13.8	171.0	60.0	64.8	15.5	3.3	194.0
*Minimum	101.0	7.2 6.6	93.0 92.0	31.1 5.8	6.8 6.8	2.8	0.4	80.4 66.4
Two Years Old—Average	104.9	11.6	144.7	51.9	54.0	10.5	2.2	112.4
Maximum	109.0	16.7	199.0	75.6	75.1	18.7	5.7	214.0
*Minimum	100.0	8.8 8.6	121.0	44.3 11.0	41.5 31.2	5.4	0.7	83.4 82.2
Three Years Old—Average	107.7	13.2	171.4	62.7	61.5	12.5	1.5	112.7
Maximum	112.0	18.3	224.0	81.8	79.8	20.8	6.1	202.0
*Minimum	104.0	11.4 10.1	145.0 119.0	52.3 16.4	47.6 34.3	6.5	0.7	79.0 60.0
Four Years Old—Average	112.2	14.0	185.0	65.9	69.3	13.9	2.8	125.1
Maximum	118.0	18.9	238.0	83.8	89.1	22.1	6.7	203.5
*Minimum	105.0	11.6 11.3	156.0 153.0	58.6 17.3	57.7 36.3	6.4	0.7	83.8 67.8
Eight Years Old—Average	123.8	18.6	256.0	82.9	89.1	16.0	3.4	154.2
Maximum	132.0	24.2	339.0	112.0	126.6	26.5	9.2	280.3
*Minimum	112.0	13.8 13.7	214.0 200.0	73.7 31.7	68.4 40.9	7.9	0.8	109.0 107.1
Bourbon Whiskey—								
New—Average	101.0	0.0	26.5	10.0	18.4	3.2	0.7	100.9
Maximum	104.0	0.0	161.0	29.1	53.2	7.9	2.0	171.3
*Minimum	100.0	0.0	4.0	12.0	13.0	1.0	trace	71.3 42.0
One Year Old—Average	101.8	7.1	99.6	41.1	28.6	5.8	1.6	110.1
Maximum	103.0	10.9	193.0	55.3	55.9	8.6	7.9	173.4
*Minimum	100.0	5.4 4.6	61.0 54.0	24.7 7.2	17.2 10.4	2.7	trace	58.0 42.8
Two Years Old—Average	102.2	8.6	126.8	45.6	40.0	8.4	1.6	108.9
Maximum	104.0	11.8	214.0	61.7	59.8	12.0	9.1	197.1
*Minimum	100.0	6.9 5.7	81.0 78.0	25.5 23.3	24.4 11.2	5.9	0.4	86.2 42.8
Three Years Old—Average	103.0	10.0	149.3	54.3	48.1	10.5	1.7	112.4
Maximum	106.0	13.8	245.0	64.8	73.0	22.1	9.5	221.8
*Minimum	100.0	8.9 7.0	95.0 90.0	38.4 32.1	27.2 12.1	5.9	0.6	88.0 43.5
Four Years Old—Average	104.3	10.8	151.9	58.4	53.5	11.0	1.9	123.9
Maximum	108.0	14.8	249.0	73.0	80.6	22.0	9.6	237.1
*Minimum	100.0	8.6 7.4	101.0 92.0	40.4 40.4	28.2 13.8	6.9	0.8	95.0 43.5
Eight Years Old—Average	111.1	14.2	210.3	76.4	65.6	12.9	2.1	143.5
Maximum	124.0	20.9	326.0	91.4	93.6	28.8	10.0	241.8
*Minimum	102.0	12.3 10.5	152.0 141.0	64.1 53.7	37.7 22.1	8.7	1.0	110.0 47.6

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*Minimum and next to minimum.

Oenanthic ether gives the chief flavor to pure cognac.

When brandy is just made it is colorless. After storing the liquor, it dissolves out of the oaken casks extractives that impart color and flavor.

The analysis, by Vasey, of cognac, and of brandy adulterated with neutral spirits, is given below.

	Cognac 10 yrs. old	Brandy mixed with neutral spirits.
Volatile acids	74.5	79.4 grams per 100 liters
Esters	109.3	32.4 grams per 100 liters
Aldehydes	16.6	7.4 grams per 100 liters
Furfural	1.7	0.6 grams per 100 liters
Fusel oil	124.2	49.0 grams per 100 liters

The following are the standards of the A. O. A. C. and the A. S. N. F. D. D. New brandy is a properly distilled spirit made from wine and contains in 100 liters of proof spirit not less than 100 grams of the volatile flavors, oils, and other substances derived from the material from which it is made, and of the substances congeneric with ethyl alcohol producing during fermentation, and carried over at the ordinary temperatures of distillation, the principal part of which consists of the higher alcohols estimated as amylic.

TABLE III.

	Alcohol per cent by volume.	Grams per 100 Liters								
				Acids						
		Extract.	Ash.	Total.	Fixed.	Volatile.	Esters.	Aldehydes.	Furfural.	Fusel Oil.
Neutral spirits	94.0	2.4	0.0	7.2	0.0	7.2	26.4	6.0	trace	28.0
Imitation whisky, rye	40.1	366.4*	4.4	43.2	9.0	34.2	3.5	trace	0.4	....
Imitation whisky, malt	45.8	854.0*	2.0	20.4	3.0	17.4	14.0	trace	1.0	37.0
Imitation whisky, rye	45.0	456.0*	5.5	9.6	3.0	6.6	5.2	trace	0.8	42.3

*Includes caramel color.

Brandy (potable brandy) is new brandy stored in wood for not less than four years without any artificial heat save that which may be imparted by warming the store house to the usual temperature, and contains in a 100 liters of proof spirit not less than 150 grams of the substances found in new brandy, save as they are changed or eliminated by storage, and of those produced as secondary products during aging; and, in addition thereto, the substances extracted from the casks in which it has been stored. It contains, when prepared for consumption, as permitted by the regulations of the Bureau of Internal Revenue, not less than 45 per cent by volume of ethyl alcohol, and, if no statement is made concerning its alcoholic strength, it contains not less than 50 per cent by volume of ethyl alcohol as prescribed by law.

Cognac, cognac brandy, is brandy produced in the department of the Charente and Charente Inferieure, France, from wine produced in those departments.

U. S. Pharmacopia Standards.—According to the U. S. Pharmacopia brandy should be at least four years old; its specific gravity should be not more than 0.941 nor less than 0.925; its alcoholic content should be from 39 to 47 per cent by weight; the residue from 100 c.c. should not exceed 0.5 gram, and should dissolve readily in 10 c.c. of cold water, and this solution should not be colored deeper than a pale green by the addition of dilute ferric chloride solution (absence of more than traces of tannin); the residue should not be sweet nor spicy in taste; a marked disagreeable pungent odor of fusel oil should not manifest itself on the volatilization of the last traces of alcohol in evaporating for the residue; in acidity, not more than 1 c.c. of tenth normal alkali should be required to neutralize 100 c.c. of the brandy, using litmus as an indicator.

Much of the brandy on the market is adulterated and has for its basis alcohol reduced to the strength required by law, flavored by rum, prune juice, syrup of raisins, acetic ether, œnanthic ether, infusion of green walnut-hulls, balsam of Tolu, Catechu, bitter almond shells, and by real brandy.

Fleischman gives a recipe below for a cheap brandy:
Spirits, 45 gals.
Coloring (carmel), 6 ozs.
Cognac oil, ⅛ oz.

Cognac oil is made up of melted cocoanut oil 16 ozs., sulphuric acid 8 ozs., alcohol 16 ozs., mixed and distilled.

Genuine new brandy may be aged or improved for immediate use according to Duplais, by adding to 100 liters the following:

Old rum	2 liters
Old Kirsch	1.75 liters
Infusion of walnut-hulls	.75 liters
Syrup of raisins	2.00 liters

Sugar and carmel are frequently found as adulterants. Whenever water or ethyl alcohol has been added, the lack of flavor resulting by the dilution is made up by the addition of cognac essences containing aromatic compounds as named above.

RUM.

Liquor distilled from fermented molasses or cane juice or from the scum and other wasted juices from the manufacture of raw sugar is called rum. The molasses wort is mixed with the residue from a previous fermentation and allowed to ferment for a number of days, after which it is distilled twice and stored in wood for a long time to remove the disagreeable odor, which is especially strong in the new product. A mixture of butyric and acetic ether, principally the former, give the characteristic flavor to old rum. To impart a fruity flavor pineapples and quavas are often put in. The best varieties of rum come from Jamaica and Vera Cruz.

The following analysis of rum is by Vasey:

Volatile acids	28.0 grams per liter
Esters	399.0 grams per liter
Aldehydes	8.4 grams per liter
Furfural	2.8 grams per liter
Fursel oil	90.6 grams per liter

The following are the joint standards of the A. O. A. C. and the A. S. N. F. D. D.: New rum is properly distilled spirit made from the properly fermented, clean, sound molasses from the massacuite, or any sound, clean, intermediate product save sugar, and contains in 100 liters of proof spirit not less than 100 grams of the volatile flavors, oils, and other substances derived from the materials which it is made, and of the substances congeneric with the ethyl alcohol producing during fermentation, which are carried over at the ordinary temperature of distillation, the principal part of which is higher alcohols estimated as amylic.

Rum (portable rum) is new rum stored not less than four years in wood without any artificial heat save that which may be imparted to the storehouse to the usual temperature, and contains in 100 liters of proof spirits not less than 175 grams of the substances found in new rum, save as they are changed or eliminated by storage, and of those produced as secondary bodies, during aging; and, in addition thereto, the substances extracted from the casks. It contains, when prepared for consumption as permitted by the regulations of the Bureau of International Revenue, not less than 45 per cent by volume of ethyl alcohol, and if no statement is made concerning its alcoholic strength, it contains not less than 50 per cent by volume of ethyl alcohol as prescribed by law.

Fictitious rum is often sold on the market made up of alcohol diluted to proper strength, with caramel added for coloring, and flavored by the addition of "rum essence." Prune juice is also added.

Fleischman gives the following recipe for low grade rum:

Spirits	40 gallons
New England Rum	5 gallons
Prune juice	½ gallon
Caramel	12 ounces
Rum essence	8 ounces

Rum essence in made up by distilling 32 ozs. of a mixture of 2 ozs. black oxide of manganese, 4 ozs. pyroligneous acid, 32 ozs. of alcohol, and 4 ozs. sulphuric acid. To this is added 32 ozs. of acetic ether, 8 ozs. of butyric ether, 16 ozs. saffron extract, and ⅛ oz. oil of birch.

GIN.

Gin is an alcoholic liquor, flavored with the volatile oil of juniper and sometimes with other aromatic substances, such as coriander, grains of paradise, anise, cardamon, orange peel, and fennel.

Schiedam schnapps (named from the town Schiedam, Holland) is a very choice variety. In this town there are nearly 200 distilleries devoted to the manufacture of gin. For this variety a mash of malted barley and rye is fermented, then distilled and redistilled in pot stills with juniper berries and sometimes hops.

Gin is water white and is kept so by storing in glass.

Much of the commercial gin is made by redistilling corn or grain whisky with oil of juniper, and often with one or more of the above flavoring materials. Sugar is added and in cheaper products oil of turpentine is substituted for juniper oil. The most characteristic flavor of gin is due to the juniper berries.

The following analysis of unsweetened gin is by Vasey:

Volatile acids	0.0 grams per liter
Esters	37.3 grams per liter
Aldehydes	1.8 grams per liter
Furfural	0.0 grams per liter
Fusel oil	44.6 grams per liter

Thirty-three samples of gin purchased by the State Board of Health of Massachusetts in saloons of the state in 1894 gave the following result in per cent of alcohol by weight:

Maximum	42.5
Minimum	29.5
Mean	38.2

LIQUEURS AND CORDIALS.

These are manufactured beverages usually high in alcohol and sugar. They are flavored with a wide variety of aromatic herbs or essences and often strongly colored. For the red colors cochineal, cudbear, red sandal, and Brazil woods are used; for the yellow colors caramel and saffron-yellow are employed; for blue, indigo; and for green, chlorophyl and malachite green.

Among the best known liqueurs and cordials are: Chartreuse, Bénédictine, Absinthe, Curaçoa, Angostura, Maraschino, Noyau or Crême de Noyau, and Crême de Menthe.

Chartreuse and Bénédictine derive their names from certain European monasteries in which these liqueurs have been made for years. Their exact method of preparation is more or less kept secret. They contain with alcohol and water much sugar, and are flavored with the volatile oils of angelica hyssop, nutmeg, and peppermint.

Absinthe is made by redistilling 40 per cent alcohol in which wormwood, anise, sweet flag and marjoram leaves have been macerated. Corlander and fennel are also used occasionally. Absinthe is highly intoxicating.

Curaçoa is made by distilling dilute spirits in which Curaçoa, orange peel, cinnamon, and other spices have been soaked. Sugar is then added to the resultant liqueur. A recipe for Curaçoa by De Brevans is given below:

Rasped skins of oranges	18 or 20
Cinnamon	4 grams
Mace	2 grams
Alcohol (85%)	5 liters
White sugar	1,750 grams

After macerating the above for fourteen days, distill without rectification, and color with caramel.

Angostura is a liqueur that has been flavored with angostura bark and various spices.

Maraschino is made by fermenting the juice of sour Italian cherries to which honey has been added. It is more commonly made by distilling a mixture in alcohol of ripe wild cherries, raspberries, cherry leaves, peach, nuts, and orris. Sugar is then added.

Noyau, or Crême de Noyau, is distilled from brandy, bitter almonds, nutmeg and mace. Sugar and coloring is then added.

De Brevaus gives a recipe for preparing Crême de Menthe by distilling a mixture of the following:

Peppermint	600 grams
Balm	40 grams
Sage	10 grams
Cinnamon	20 grams
Orris root	10 grams
Ginger	15 grams
Alcohol (80%)	50.30 cc.

producing finally 10 liters of the liquor, after which 3.750 grams of white sugar are added. The better grades of Crême de Menthe were colored by an alcoholic solution of chlorophyll, derived by macerating bruised green leaves of various plants with alcohol. At present coal tar dyes are being used.

Table IV shows an analysis of the best known cordials by König:

TABLE IV.

	Specific gravity.	Alcohol by volume.	Alcohol by weight.	Extract.	Cane sugar.	Other extractives.	Ash.
Absinthe	0.9116	58.93	....	0.18	.....	0.32	.....
Bénédictine	0.0709	52	38.5	36.0	32.57	3.43	0.043
Ginger	1.0481	47.5	36.0	27.79	25.92	1.87	0.141
Crême de Menthe	1.9447	48.0	36.5	28.28	27.63	0.65	0.068
Anisette de Bordeaux	1.0847	42.0	30.7	34.82	37.44	0.38	.....
Curaçoa	1.0300	55.0	42.5	28.60	28.50	0.10	.....
Kummel	1.0830	33.9	24.8	32.02	31.18	0.84	.....
Angostura	0.9540	49.7	....	5.85	4.16	1.69	.....
Chartreuse	1.0799	43.18	....	36.11	34.35	1.76	.....

METHODS OF ANALYSIS OF DISTILLED LIQUORS.

Specific Gravity.—This should be taken at 15.6° C.; if not, it should be calculated to that temperature. It is determined by a hydrometer spindle in a glass cylinder, Westphal balance, or by the pycnometer. The latter is by far the most accurate.

Extract.—Weigh or measure at 15.6° C. 1000 c.c. of the sample, place on water bath and evaporate nearly to dryness, then put in a water oven and dry at the temperature of boiling water for two and a half hours.

Determination of Acids.—Titrate a 100 c.c., if sample is dark in color dilute 50 c.c. to 100, with tenth normal alkali, using phenolphthalein as indicator. 1 c.c. of tenth normal alkali is equal to 0.006 grams of acetic acid.

Determination of Esters.—200 c.c. of sample are diluted with 25 c.c. of water and distilled slowly into a graduated 200 c.c. flask until nearly filled to mark. Complete the volume, shake, and use aliquot portions for the determination of esters, aldehydes, and furfural.

50 c.c. of the distillate are exactly neutralized with tenth-normal alkali, using phenophthalein as an indicator, and add 25 to 50 c.c. of the tenth-normal alkali in excess of that required for neutralization. Either stand over night and then boil with a tube condenser for one-half hour below the boiling point, or boil one hour with a reflux condenser, cool, and titrate with tenth-normal acid, using phenophthalein as indicator. Multiply the number of c.c. of the tenth-normal alkali used in the saponification by .0088, thus obtaining the grams of esters calculated as ethyl acetate.

Determination of Aldehydes.—Reagents—(a) prepare alcohol free from aldehydes by redistilling the ordinary 95 per cent alcohol over potash or caustic soda, then add from 2 to 3 grams per liter of m-phenylenediamine hydrochloride, heat, using either reflux condenser or steam bath or digest at ordinary temperature for several days, and then distill slowly, rejecting the first 100 c.c. and the last 200 c.c.

(b) Sulphite—fuchsin solution—Dissolve 0.50 grams of pure fuchsin in 500 c.c. of water, then add 5 grams of SO_2 dissolved in water, make up to a liter and allow to stand until colorless. This solution retains its strength for but a few days and therefore should be made up in small quantities.

(c) Standard Acetic Aldehyde Solution.—Vasey gives a preparation as follows: Grind aldehyde ammonia in a mortar with ether, and decant the ether. Repeat this operation several times then dry the purified salt in a current of air and finally in a vacuum over sulphuric acid. Dissolve 1.386 grams of this purified ammonium aldehyde in 50 c.c. of 95 per cent alcohol, to this add 22.7 c.c. of normal alcoholic sulphuric acid, then make up to 100 c.c. and add 0.8 c.c. to compensate for the volume of the ammonium sulphate precipitate. Allow this to stand over night and and filter. This solution contains one gram of acetic aldehyde in 100 c.c. and will retain its strength.

The standard found most convenient for use is 2 c.c. of this strong aldehyde solution diluted to 100 c.c. with 50 per cent alcohol by volume. One c.c. of this solution is equal to 0.0002 gram of acetic aldehyde. This solution should be made up fresh every day or so, as it loses its strength. Process: The aldehyde is determined from the distillate prepared for esters. 5 to 10 c.c. of the distillate are diluted to 50 c.c. with aldehyde free from alcohol (50 per cent by volume), add 25 c.c. of the fuchsin solution, and allow to stand for fifteen minutes at 15° C. The solution and reagents should be at 15° C. before they are mixed. The standards of known strength are prepared the same way.

Determination of Furfural.—Standard furfural solution is made by dissolving 1 gram of redistilled furfural in 100 c.c. of 95 per cent alcohol. This is a strong solution and will keep. Standards are made by diluting 1 c.c. of this solution to 100 c.c. with 50 per cent of volume of alcohol. One c.c. of this solution contains 0.0001 gram furfural. Process: Dilute from 10 to 20 c.c. of the distillate, prepared as described under esters, to 50 c.c. with furfural-free alcohol (50 per cent by volume) and 2 c.c. of colorless anilin to this and 0.5 c.c. of hydrochloric acid (Sp. gr. 1.125) and keep for fifteen minutes in a water bath at about 15° C. Prepare standards of known strength in the same way.

Detection of Fusel Oil.—Odor Test: Dealcoholize a liquor in an open dish on the water bath. When the last traces of alcohol are going off and fusel oil is present the latter gives off a harsh nauseating odor. It causes an uncontrollable desire to cough. Pour a small quantity of the spirit into the hand and allow to evaporate slowly or rinse out a warm beaker with the liquor and observe the odor in each case. Goebel gives the following test based on the detection of volatile acids: 30 c.c. of the liquor are agitated with 2 or 3 c.c. of a dilute solution of potassium hydroxide; evaporate over the water bath to the volume of 2 or 3 c.c., cool, and to the residue add 5 or 6 c.c. of concentrated sulphuric acid. If fusel oil be present, the characteristic odors of valerianic and butyric acids will be present.

Determination of Fusel Oil.—Allen Marquard Method: Add to 100 c.c. of whisky 20 c.c. of half-normal sodium hydroxide and saponify the mixture by boiling for one hour under a reflux condenser. Connect the flasks with a distilling apparatus, distill 90 c.c., add 25 c.c. of water, and continue the distillation until an additional 25 c.c. is collected.

Approximately saturate the distillate with finely ground sodium chloride and add a saturated solution of sodium chloride until the specific gravity is 1.10.

Extract this salt solution four times with pure carbon tetrachloride using 40, 30, 20 and 10 c.c. respectively, and wash the carbon tetrachloride three times with 50 c.c. portions of a saturated solution of sodium chloride, and twice with a solution of saturated sodium sulphate. Then transfer the carbon tetrachloride to a flask containing 5 c.c. of concentrated sulphuric acid, 45 c.c. of water, and 5 grams of potassium bichromate, and boil for eight hours under a reflux condenser.

Add 30 c.c. of water and distill until only about 20 c.c. remain; add 80 c.c. of water and distill until 5 c.c. are left. Neutralize the distillate to methyl orange, and titrate with sodium hydroxide, using phenolphthalene as indicator. One c.c. of tenth-normal sodium hydroxide is equivalent to 0.0088 gram of amyl alcohol.

Rubber stoppers can be used in the saponification and first distillation, but corks covered with tinfoil must be used in the oxidation and second distillation; corks and tinfoils must frequently be renewed.

Mitchel and Smith Method for Determining Fusel Oil.—This method is more rapid than the Allen-Marquardt method, and gives more nearly the true amount of fusel oil.

Saponify, distill, shake with sodium chloride and extract with carbon tetrachloride, as in the Allen-Marquardt method. To the carbon tetrachloride extract, contained in the separatory funnel, add 10 c.c. of potassium hydroxide solution (1:1). Cool the mixture in ice water to approximately 0° C. Similarly cool 100 c.c. of a solution of potassium permanganate solution (20 grams to the liter), accurately measured in a flask. To the contents of the separatory funnel add the bulk of the permanganate solution, but without rinsing, retaining the residue to be added at a later stage. Remove the mixture from the bath and shake vigorously for five minutes; set aside for thirty minutes, with occasional shaking, permitting the liquid to warm to room temperature (20 to 25° C.).

Accurately measure into a liter Erlenmeyer flask 100 c.c. of a solution of hydrogen peroxide slightly (about 2 per cent) stronger than the permanganate solution, acidulate with 100 c.c. of an approximately 25 per cent sulphuric acid solution, and slowly add the contents of the separatory funnel with constant shaking, keeping the acid solution constantly in excess. Rinse the separatory funnel and the flask containing the residue of permanganate with water and add to the peroxide solution. Finally titrate the excess of hydrogen peroxide with standard potassium permanganate (10 grams to the liter). Run a blank determination, using the same amounts of the stronger permanganate, potassium hydroxide, hydrogen peroxide, and sulphuric acid solutions, and titrating the residual peroxide with the standard potassium permanganate as before. The difference in the amounts of the permanganate consumed, in grams, times 0.696, gives the amount as before.

Detection of Methyl Alcohol.—Leach & Lythgoe Immersion Refractometer Method: Determine at 20° C. the refraction of the distillate obtained in the determination of alcohol by the immersion refractometer. If on reference to the table the refraction shows the percentage of alcohol agreeing with that obtained from the specific gravity, it may safely be assumed that no methyl alcohol is present. If, however, there is an appreciable amount of methyl alcohol, the low refractometer reading will at once indicate the fact. If the absence of other refractive substances than water from the solution is assured, this qualitative test by difference in refraction is conclusive.

The addition of methyl to ethyl alcohol decreases the refraction in direct proportion to the amount present; hence the quantitative calculation is readily made by interpolation in the tables, using the figures for pure ethyl and methyl alcohol of the same alcoholic strength as the sample.

Example—Suppose the distillate made up to the original volume of the measured portion taken for the alcohol determination has a specific gravity of 0.9736, corresponding to 18.38 per cent alcohol by weight, and has a refraction of 35.8 at 20° C. by the immersion refractometer; by interpolation in the refractometer table the readings of ethyl and methyl alcohol corresponding to 18.38 per cent alcohol are 47.2 and 25.4 respectively, the difference being 21.8; 47.2 — 35.8 = 11.4; (11.4 ÷ 21.8) 100 = 52.3, showing that 52.3 of the alcohol present is methyl alcohol.

TABLE V.—SCALE READINGS ON ZEISS IMMERSION REFRACTOMETER AT 20° C., CORRESPONDING TO EACH PER CENT BY WEIGHT OF METHYL AND ETHYL ALCOHOL.

	Scale Readings.			Scale Readings.			Scale Readings.			Scale Readings.	
Per cent Alcohol by Weight.	Methyl Alcohol.	Ethyl Alcohol.	Per cent Alcohol by Weight.	Methyl Alcohol.	Ethyl Alcohol.	Per cent Alcohol by Weight.	Methyl Alcohol.	Ethyl Alcohol.	Per cent Alcohol by Weight.	Methyl Alcohol.	Ethyl Alcohol.
0	14.5	14.5	26	30.3	61.9	51	39.7	91.1	76	29.0	101.0
1	14.8	16.0	27	30.9	63.7	52	39.6	91.8	77	28.3	100.9
2	15.4	17.6	28	31.6	65.5	53	39.6	92.4	78	27.6	100.9
3	16.0	19.1	29	32.2	67.2	54	39.5	93.0	79	26.8	100.8
4	16.6	20.7	30	32.8	69.0	55	39.4	93.6	80	26.0	100.7
5	17.2	22.3	31	33.5	70.4	56	39.2	94.1	81	25.1	100.6
6	17.8	24.1	32	34.1	71.7	57	39.0	94.7	82	24.3	100.5
7	18.4	25.9	33	34.7	73.1	58	38.6	95.2	83	23.6	100.4
8	19.0	27.8	34	35.2	74.4	59	38.3	95.7	84	22.8	100.3
9	19.6	29.6	35	35.8	75.8	60	37.9	96.2	85	21.8	100.1
10	20.2	31.4	36	36.3	76.9	61	37.5	96.7	86	20.8	99.8
11	20.8	33.2	37	36.8	78.0	62	37.0	97.1	87	19.7	99.5
12	21.4	35.0	38	37.3	79.1	63	36.5	97.5	88	18.6	99.2
13	22.0	36.9	39	37.7	80.2	64	36.0	98.0	89	17.3	98.9
14	22.6	38.7	40	38.1	81.3	65	35.5	98.3	90	16.1	98.6
15	23.2	40.5	41	38.4	82.3	66	35.0	98.7	91	14.9	98.3
16	23.9	42.5	42	38.8	83.3	67	34.5	99.1	92	13.7	97.8
17	24.5	44.5	43	39.2	84.2	68	34.0	99.4	93	12.4	97.2
18	25.2	46.5	44	39.3	85.2	69	33.5	99.7	94	11.0	96.4
19	25.8	48.5	45	39.4	86.2	70	33.0	100.0	95	9.6	95.7
20	26.5	50.5	46	39.5	87.0	71	32.3	100.2	96	8.2	94.9
21	27.1	52.4	47	39.6	87.8	72	31.7	100.4	97	6.7	94.0
22	27.8	54.3	48	39.7	88.7	73	31.1	100.6	98	5.1	93.0
23	28.4	56.3	49	39.8	89.5	74	30.4	100.8	99	3.5	92.0
24	29.1	58.2	50	39.8	90.3	75	29.7	101.0	100	2.0	91.0
25	29.7	60.1									

Trillat Method—To 50 c.c. add 50 c.c. of water and 8 grams of lime, and fractionally distill by the aid of Glinsky bulb tubes. Dilute the first 15 cc. of the distillate to 150 c.c., mix with 15 grams of potassium bichromate and 70 c.c. of sulphuric acid (1:5), and allow to stand for one hour with occasional shaking.

Distill, reject the first 25 c.c. and collect 100 c.c. Mix 50 c.c. of the distillate with 1 c.c. of rectified dimethylanilin, transfer to a stout tightly-stoppered flask, and keep on bath at 70° to 80° C. for three hours with occasional shaking. Make distinctly alkaline with sodium hydroxide, and distill the excess of dimethyl-anilin, stopping the distillation when 25 c.c. have passed over.

Acidify the residue in the flask with acetic acid, shake, and test a few c.c. by adding four or five drops of water with lead dioxide in suspension (1 gram in 100 c.c.). If methyl alcohol be present, a blue coloration occurs which is increased by boiling.

Note.—Ethyl alcohol thus treated yields a blue coloration, changing immediately to green, afterwards to yellow and becoming colorless when boiled.

Detection of Caramel.—Crampton and Simon's Method—Evaporate 50 c.c. of the liquid nearly but not quite to dryness in an evaporating dish on the water bath. Wash with water into a 50 c.c. graduated glass stoppered flask, add 25 c.c. of absolute alcohol, and fill to the mark with water. Shake, and transfer 25 c.c. to a separatory funnel of the type the stem of which terminates in a 25 c.c. graduated bulb pipette, provided with a stop cock.

Add 50 c.c. of ether and shake carefully at intervals during a half an hour. After complete separation, make up the lower aqueous layer with water to the 25 c.c. mark, which may be done by siphoning it in through a rubber tube from an elevated flask, controlling the supply by stop cocks. Shake the separatory funnel, and again allow the layers to separate, draw off the aqueous layer, and compare with the color of the original liquor. Express the amount of color removed as per cent of the total amount. Ether will readily dissolve the natural color due to oakwood (mainly flavescin) while caramel is insoluble in ether; hence uncolored liquors are partially decolorized by this treatment, while those colored with caramel show little change.

Amihor test, modified by Laschi—Add 10 c.c. of paraldehyde to 5 c.c. of the sample contained in a test tube and shake. Add absolute alcohol, a few drops at a time, shaking after each addition until the mixture becomes clear. Allow to stand. Turbidity after ten minutes is an indication of caramel.

Determination of Water Insoluble in Whiskeys.—50 c.c. of sample are evaporated to just dryness. Approximately 15 c.c. of water are used to then take up the residue and filter, wash until about 25 c.c. of filtrate are collected. 25 c.c. of absolute or 26.3 c.c. of 95 per cent by volume alcohol are added to make up to 50 c.c. The solution is mixed thoroughly and compared with the original sample in a colorimeter. The per cent of color insoluble in water is calculated from these readings.

Determination of Color Insoluble in Amyl Alcohol.—Modified Marsh Test: Evaporate 50 c.c. of whisky just dryness on the steam bath. Add 26.3 c.c. of 95 per cent alcohol to dissolve the residue. Transfer to a 50 c.c. flask and make up to a volume with water to obtain a uniform alcohol concentration. Place 25 c.c. of this solution in a separatory funnel, and add 20 c.c. of the Marsh reagent, shaking lightly so as not to form an emulsion (reagents consists of 100 c.c. of pure amyl alcohol, 3 c.c. of syrupy phosphoric acid, and 3 c.c. of water; shake before using) allow the layers to separate, repeat this shaking and standing twice again. After the layers have clearly separated, draw off the lower or watery layer which contains the caramel into a 25 c.c. graduated cylinder and make up to volume by 50 per cent by volume alcohol. Compare this solution in a colorimeter with the untreated 25 c.c. Calculate the result to this reading to the per cent of color insoluble in amyl alcohol.

Analysis of Cordials and Liqueurs.—No regular systematic plan can be made for identification due to the wide variety of essences and flavoring principals used. Coloring matters, acids, sugars, and alcohol are determined similarly as in other liquors, except that in case of alcohol all volatile oils must be first separated out. The presence of volatile oils is shown if a precipitate is formed on treatment of a sample with few c.c. of water in a test tube.

The sense of smell and taste is highly useful both in applying to the liqueur itself or to the dry extract for suggestions as to the main ingredients employed.

A RAPID METHOD FOR DETERMINATION OF ESSENTIAL OILS IN ALCOHOL.[*]

By W. B. D. PENNIMAN and W. W. RANDALL.[†]

As the result of series of experiments carried out in this laboratory at intervals during several years, a method has been devised for the assay of spirits of camphor and of peppermint, and of the extracts of lemon, orange, peppermint, anise and nutmeg, which appears to be more rapid and much more accurate than any method with which we are familiar. The facts which form the basis of the method may be grouped under three heads, as follows:

1. Camphor and the several oils enumerated above are completely expelled from solution in alcohol, when these solutions are mixed with from four to ten volumes of a strong solution of calcium chloride.

2. The separated camphor or oil dissolves with the greatest ease in low-boiling gasoline, an operation with which alcohol, at least in the presence of such a calcium chloride solution, does not interfere.

3. Within certain fairly wide limits, the volume of the gasoline solution formed is exactly equal to the sum of the volumes of the gasoline itself and the solid camphor (or oil) which has been dissolved.

The method here described is by no means entirely new. Schmatolla[1] noted that when camphor dissolves in light petroleum oil, the volume-relation stated in "3" obtains. He employed a burette graduated in tenths cc. as a measuring apparatus, and weighed out the camphor spirit, which was later precipitated by means of saturated sodium chloride solution. We have secured better results by the use of calcium chloride solution, and preter graduated milk bottles and the use of the centrifuge as means of accurate measurement of small quantities. Arnost[2] used a somewhat similar method to determine camphor in celluloid, correcting for alcohol dissolved. Chittick[3], we have found since these experiments were made, used a method similar to ours for peppermint, precipitating the oil with water and, by means of a blank, correcting for alcohol dissolved. We have not found water a satisfactory precipitant, and believe that much time can be saved without decrease in accuracy by the use of pipettes and the avoidance of weighings.

The apparatus called for consists simply of several accurate full pipettes, a Babcock centrifuge, and one or more accurately graduated Babcock milk bottles. If the divisions on the neck of the bottle be from 0 to 10, then the graduated portion will contain just 2 cc. With a magnifying glass the volume of a column of supernatant solution in the neck of the bottle can be read with accuracy, probably to 0.008, perhaps to 0.004 cc.

As the volume of gasoline used should not be much less than, nor much more than twice as great as that of the camphor or oil to be dissolved (if the volume-relation mentioned under "3" is to hold good), it is well to work with such quantities that not much over 0.5 cc. of camphor or oil is to be determined. Thus we have found that 5 cc. of the alcohol solution serves well for strengths from 5 to 15 per cent; 10 cc. is probably better for 4 per cent solutions or anything weaker. The quantity of gasoline should in general be somewhat greater than that of the oil.

ALCOHOL DISTILLERIES IMPORTANT TO GERMAN AGRICULTURE.

The importance that alcohol distilleries may assume in scientific agriculture is pointed out in a recent professional paper published by the United States Department of Agriculture under the title of "Agricultural Alcohol; Studies of Its Manufacture in Germany." The results of the author's study indicate that the manufacture of alcohol for technical purposes, not for human consumption, is not regarded in itself as a profitable business but as a necessary factor in general farming. The distilleries provide a market for Germany's enormous potato crop, which in turn has made possible the profitable cultivation of large tracts of light sandy soil in the east. The spent mash again is returned to the farmers from the distilleries and used as feed for cattle which furnish manure for the enrichment of the soil. On account of the pressure of the population and the desire to cultivate as large an acreage as possible, German farmers have not been raising as much live stock as would be good agricultural practice, and anything that tends to stimulate them in this direction is regarded as most desirable.

Approximately 6,000 agricultural potato distilleries are now in operation in the German empire. Many of these are co-operative distilleries in which it is interesting to note that the co-operators do not hold shares having a certain money value, but possess the privilege of calling daily for a certain quantity of spent mash. To the potato crop itself an eighth of the arable land in the German empire is now devoted, and the production is enormous.

In some instances crops of more than 535 bushels per acre have been harvested, while yields of 300 to 375 bushels are quite common.

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[*] From the Journal of Industrial and Engineering Chemistry.

[†] Of the State Health Department, Baltimore, Md.

[1] Apoth. Zeit., 16, 290; Abstr. Chem. Centr., 1901, 1 (20), 1117; J. Soc. Chem. Ind., 20 (1901), 756; Allen's "Commercial Organic Analysis" (new ed.), Vol. IV, p. 200.

[2] Z. Unter. Nahr. u. Genussm., 12 (1906), 532; Abstr. J. Soc. Chem. Ind., 25, 1169.

[3] Proc. Assn. Am. Dairy, Food and Drug Off., 1913, p. 160; Abstr. Chem. Abstr., 8 (1914), 1847.

METALLURGY

THE MICROSCOPIC STRUCTURE OF HIGH-SPEED STEELS.

By H. B. PULSIFER.

(*Conclusion.*)

Some of the more interesting large grain structures are shown in Figs. 1, 2, 3, and 4.

Fig. 1 is from steel E as quenched from 920°, a different portion of whose surface was seen in Fig. 5 of our December contribution. This latter view is from the very exterior shell where the grain is exceedingly coarse. The austenite is slightly pitted and shows a few carbide droplets, otherwise nearly a polished surface. The grain demarkations are rather wide and in places even further widened by clumps of what appears to be pearlite. Etching with the stronger acid as is necessary to best define the cell lines corrodes this pearlite so deeply that it appears black in the print.

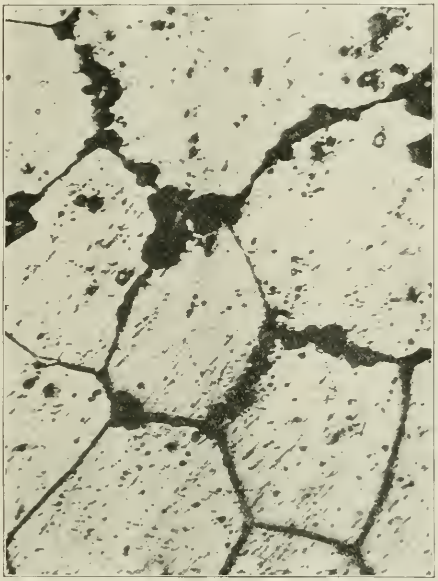


Fig. 1.

Fig. 2 is from the possibly misplaced specimen of steel F which was supposedly quenched from 1040°. In this instance the grain is the largest seen in any of the specimens. These grains of such enormous size occur in the exterior, only, and are easily of such magnitude that one of our prints might be taken of an interior without showing a trace of the grain boundary. Fig. 2 shows the grain separations thin while the interiors are heavily pitted; it appears as if the dark constituent had not yet migrated to the cell walls.

A case in which the migration of the dark constituent is wholly complete is seen in Fig. 3; this is from steel C as quenched from 1280°. The heating has necessarily been fairly long in this case. The carbides are gone, the grain has grown large and the dark masses (pearlite?) have clumped about certain grain walls. It is a very interesting coalescence. In a way it much resembles the coalescence of ferrite and carbide by over-heating when those constituents occur free in their proper conditions.

The next stage in this peculiar coalescence which accompanies the growth of the huge grains in these steels is seen in Fig. 4. Here the smooth and polished austenite has cleared of the pearlite which has clumped about the grain borders, while a carbide rib has formed through the high-carbon mass and is seen as the third factor in establishing and making plain the grain boundaries. This specimen comes from steel E as quenched from 1280°. Any steel in which this structure had penetrated sensibly would certainly have a brittleness rendering it wholly useless.

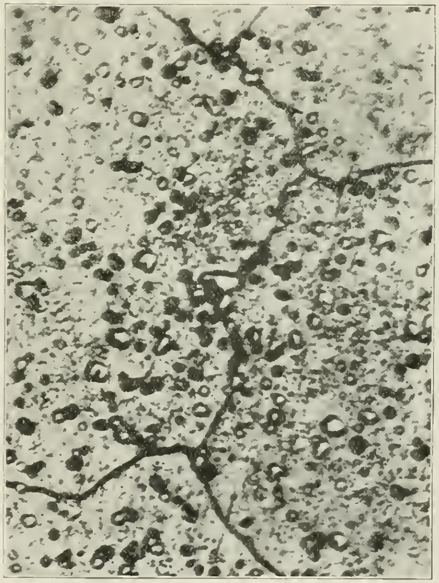


Fig. 2.

Two conspicuous and wholly distinct modes of transition from martensite to austenite are apparently

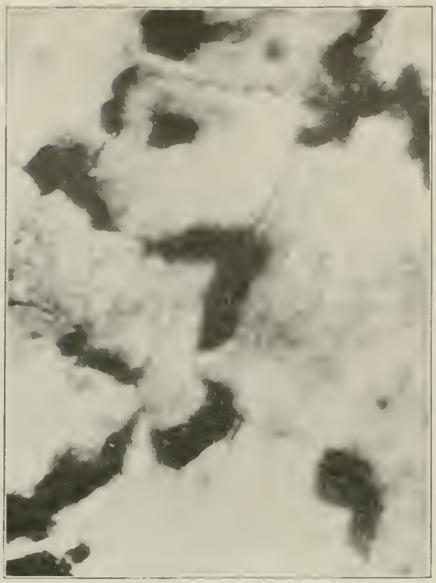


Fig. 3.

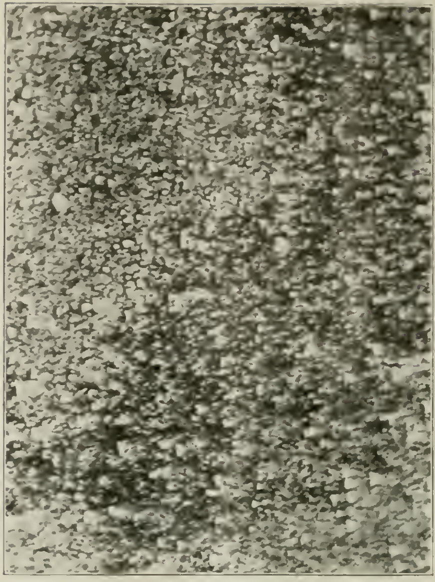


Fig. 5.

before us. First, with the heating to the required temperature it is plain that the new cellular solid solution of austenite is born throughout the martensitic mass; our prints have shown this in several cases. The many centers give rise to little grains which are uniformly and regularly distributed everywhere in the steel. The second sort of change begins at the surface and progressively penetrates toward the heart of the piece. This latter transformation has as advance preparation the formation of a pearlitic zone and a final condition of the huge pitless grains with the dark constituent clumped along the borders.

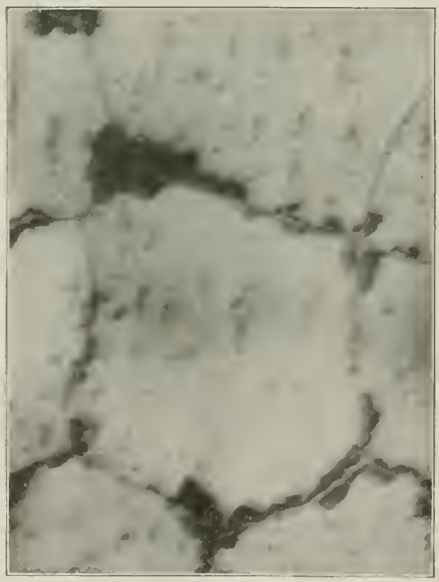


Fig. 4.

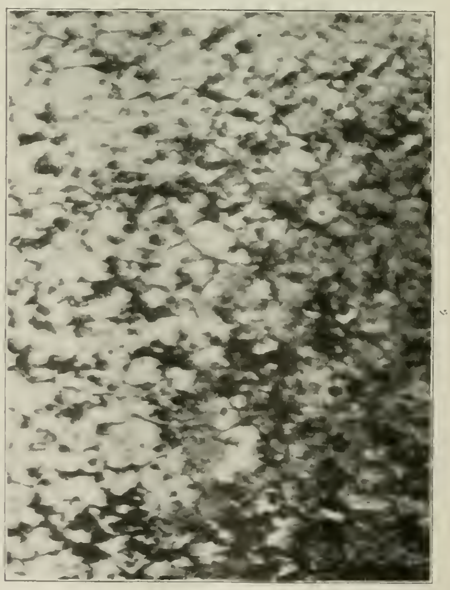


Fig. 6.

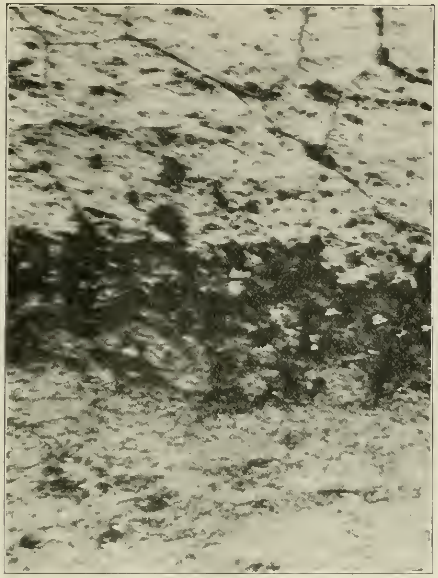


Fig. 7.

Fig. 5 indicates a wave of transition spreading through the mass. Evidently martensite is coalescing about local centers with boundaries in the making.

Fig. 6 is even more conclusive; this shows the rough cell-less martensite on one side and the well developed austenite on the other. Such prints are extremely hard to get at 500 diameters for the hardness changes so rapidly with the structure that only the most skillful polishing will give a presentable surface without the soft side pitching away so as to be out of focus. These surfaces were almost wholly ground on the smooth emery stone, subsequent smoothing to rid of scratches being reduced to the least possible. Figs. 5 and 6 are from steel E, the first quenched from 1100°, the second from 1160°.

Fig. 7 shows the pearlitic fringe advancing before the new austenite with its huge grains. This print is taken at a very narrow point in the zone; at other points the zone broadens so that the entire plate might be covered with the pearlite. One extremely interesting print in the author's possession shows a pearlitic ground with grains of each sort mixing across the space; the austenite grains smooth and bright, the martensite rough and striated; the two sorts are mixed in the struggle, some cells advanced far into and surrounded by the units of the opposite sort.

Fig. 8, which is our last print, again presents a beautiful case of the advance of the pearlitic fringe. One side is rough martensite, the other large-grained austenite; between is the broken zone with huge cells being formed, pearlite clumping together and martensite losing its nature. The two solid solutions are apparently sharply defined as to smoothness but both are badly broken by the dark masses. This last print is from steel C as quenched from 1280°.

SUMMARY.

In a general way the study demonstrates typical structures for pearlite, martensite and austenite in high-speed steels. Transitions from one to the other are described and illustrated; what happens with excessive heating of the material is also shown.

From pearlite to martensite looks like a short step accomplished largely within the molecules and sparingly portrayed in microscopic character. It is true that from softest pearlite to hardest martensite the step is easy to recognize; it is plain by scleroscope, etching and appearance; yet the pearlite is also capable of considerable hardening while it still etches and looks quite the same. Unquestionably there is a new solid solution formed with the completed change.

From martensite to austenite the steps are drawn out and accomplished with deliberation; numerous degrees may be caught and studied. The loss of gran-

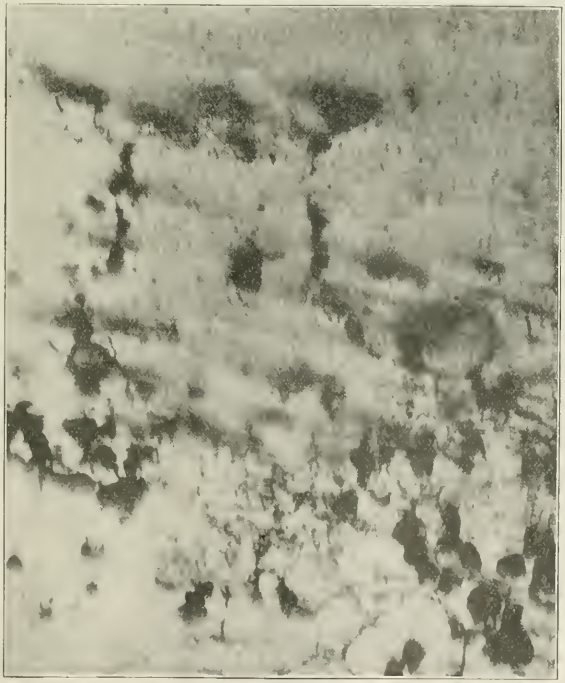


Fig. 8.

ularity by martensite and the taking of the cell form by the austenite has possibly been studied only in less detail previously.

The further grain growth of austenite and the advance of the pearlitic fringe is a novel and undescribed phenomenon. Is it the rate of heating which determines whether high carbon segregates shall be bunched along the grain boundaries, held in nodules throughout the grain, or bodily assimilated? Further investigation may answer the question, all three of the cases are plainly shown in prints.

The carbide rib through the pearlite areas of the mammoth austenite we have been taught to expect, but how shall we explain the chemistry and physics of the advance of the pearlite zone.

The best method of heat-treating high-speed steel has been demonstrated by tests too overwhelming to be in any degree controverted; the fine-grained austenitic structure has likewise long been proclaimed as the aim of heat treatment. If anything, the experiments here recorded tell us how *not* to treat the steel and throw us back on the time-honored method of soaking thoroughly at a low heat, then bringing to incipient fusion at the end and quenching. Such a course assumes that the martensite-austenite transformation takes place rather uniformly throughout the specimen while the short interval of high heat gives no chance for the appreciable advance of mammoth austenite behind its pearlitic fringe. A slight grinding of the surface will then expose fine austenite as the cutting edge for hot work.

Cold hardness is seen to be highest developed in the median martensitic stage; this ensues all the way from below 1000° to above 1100° with moderately short soaking. Some loss of cold hardness with the advance of structure toward sub-austenite and fine austenite is apparently inherent in the same and does not matter for hot work according to the best authorities.

The results are wholly in accord with the best information on the subject. The function of carbon and exact composition as regards tungsten and chromium amount to little within the limits of the composition of the steels used.

The following bibliography will be found to comprise practically all of the literature covering the chemical and structural constitution of the steels in question. Many excellent papers on physical and working tests are of course omitted:

BIBLIOGRAPHY.

1. "Microstructure of Steel Quenched from the Melting Point," by Albert Sauveur. The Metallographist, 3 (1900); p. 244.

One print of a chrome-tungsten steel at 250 diameters shows austenite and cementite and relative hardness.

2. "Les Aciers au Chrome," by L. Guillet. Revue de Metallurgie, I (1904); p. 155.

Excellent presentation of the chrome-steels.

3. "Aciers au Tungstene," by L. Guillet. Revue de Metallurgic, I (1904); p. 263.

Gives diagram of structures found and forecast, with summary of the carbides of tungsten and tungstides of iron.

4. "Les Aciers Rapides a Outils," by H. le Chatelier. Revue de Metallurgie, I (1904); p. 334.

Subject very fully discussed; diagram of a bar heated and quenched at one end, only, shows soft metal, the zone of martensite, the cellular zone and the coarse exterior produced by maximum heat. Four good prints accompany the paper. Transitions are indicated as gradual and uniform, no special zone.

5. "Contributions a la Theorie des Aciers Rapides," by F. Osmond. Revue de Metallurgie, I (1904); p. 348.

Wholly academic discussion with no work or prints

6. "The Development and Use of High-Speed Tool Steel," by J. M. Gledhill. Journal of the Iron and Steel Institute (British), LXVI (1904-II); p. 127.

Paper chiefly devoted to composition and cutting tests, but accompanied by five prints, decidedly mediocre.

7. "Comparison des Proprietes et Classification des Aciers Ternaires," by L. Guillet. Revue de Metallurgie, II (1905); p. 350.

Describes the tungsten steels as pearlitic or double carbide, and gives diagram of limiting compositions.

8. "The Types of Structure and the Critical Ranges on Heating and Cooling of High-Speed Tool Steels Under Varying Thermal Treatment," by H. C. H. Carpenter. Journal of the Iron and Steel Institute (British), LXVII (1905-I); p. 433.

Twenty-seven prints accompany this important paper. The prints at 30 diameters are of small account while the few at 1,000 diameters are only about an inch square.

9. "Recherches Recentes Faites sur les Alliages Industriels-Leur Importance," by L. Guillet. Revue de Metallurgie, III (1906); p. 155.

States that for commercial work the chrome-tungsten steels should be of fine martensitic structure with the carbides fully dissolved by long enough heating at high temperature. No illustrations.

10. "Quarternary Steels," by L. Guillet. Journal of the Iron and Steel Institute (British), LXX (1906-II); p. 1.

A most massive article. Twelve prints reduced from 200 diameters accompany. Strongly affirms that maximum hardness corresponds with total disappearance of the carbides. States that too rapid cooling gives inferior hardness due to the formation of gamma-iron. " * * * a well quenched high-speed tool steel should not reveal the pronounced presence of any constituent." Annealing only increases carbides without further alteration of structure.

11. "Tempering and Cutting Tests of High-Speed Steel," by H. C. H. Carpenter. Journal of the Iron and Steel Institute (British), LXXI (1906-III); p. 337.

Another extensive paper accompanied by twenty-five prints. Small specimens are quenched from a series of temperatures. The author notes the increasing size of the polyhedra as the temperature of quenching is raised. Magnifications are low while oxidation and scratches appear to have confused the issues.

12. "Aciers Chrome-Tungsten," by L. Guillet. Revue de Metallurgie, IV (1907); p. 5.

Describes extensive investigations; quenches from different temperatures; finds time required to dissolve carbides at various temperatures and that the hardness is greatest when such are in solution. Sixteen photomicrographs accompany.

13. "Function of Chromium and Tungsten in High-Speed Steel," by C. A. Edwards. Journal of the Iron and Steel Institute (British), LXXVII (1908-II); p. 104.

A masterly discussion of the subject accompanied by much experimental data; analyses, heating and cooling curves, hardness tests and photomicrographs.

14. "The Constitution of Carbon-Tungsten Steels," by Thomas Swinden. Journal of the Iron and Steel Institute (British), LXXX (1909-II); p. 223.

Refers mainly to the heating and cooling phenomena.

15. "The Chemical and Mechanical Relations of Iron, Chromium and Carbon," by J. O. Arnold and A. A. Read. Journal of the Iron and Steel Institute (British), LXXXIII (1911-I); p. 249.

Describes and illustrates limited areas which contain troosite, sorbite, granular and laminated pearlite.

16. "Microskopische Untersuchung einiger hochlegierten Sonderstähle," by Felix Fettweis. Stahl und Eisen, 32,2 (1912); p. 1866.

A valuable article dealing chiefly with the cast condition of the high-speed steels, showing how later structures (after working and heat treating) depend on this first condition. Thirty-six prints, 1¾ inches in diameter, at 40, 45, 50, 75, 80, 100, 350, 600, and 1,000 diameters magnification are given on three pages. Through this source the author learned of etching with sulphurous acid.

17. "Die Fortschritte deutsche Stahlwerke bei der Herstellung hochlegierte Schnellarbetisstähle," by G. Schlesinger. Stahl und Eisen, 33,1 (1913); p. 929. Rejoiner by Poldihutte, same, 33,2 (1913); p. 1196.

Mainly concerns cutting ability, but five good prints are shown and the constitution as influenced by quenching strongly brought out.

18. "Aciers a Outils," by M. Denis. Revue de Metallurgie, XI (1914); p. 4.

A massive paper on the cutting efficiency of steels, but relating specifically to the constitution of high-speed steel when it is found that varying carbon from .3 to 1.3% does not change the hot-hardness. The Herbert testing machine is used. High speed tools are tempered between 400 and 600° C. for hot cutting, with 690° as the limiting temperature above which hot-hardness acquired by quenching begins to be lost.

19. "Etude sur les Proprietes Generales des Aciers a Outils," by M. Denis. Revue de Metallurgie, XI (1914); p. 569.

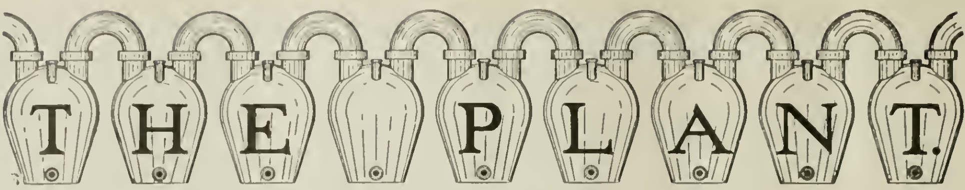
A monumental paper full of precision and new conceptions; chiefly concerning cutting tests but reflecting strongly on constitution of the high-speed steels when it is shown that variation of 100° from best quenching temperature affects hardness slightly, and that physical tests on cold samples are not correlated with greatest efficiency under hot working conditions.

20. "The Chemical and Mechanical Relations of Iron, Tungsten and Carbon, and of Iron, Nickel and Carbon," by J. O. Arnold and A. A. Read. Paper read before the Institution of Mechanical Engineers (British) March 20, 1914. Reported in the Iron and Coal Trades Review, March 27, 1914.

A very suggestive paper, emphasizing the probability of dissolved iron tungstide and the progressive hardening on quenching from 850° to 1150° C.

A DISCOVERY IN STEEL MAKING.

The U. S. Consul at Sheffield, England, under date of January 15 reports that a Sheffield firm has introduced "Tirth's stainless" steel, which it claims is non-rusting, unstainable, and untarnishable. This steel is especially adapted for table cutlery, as the original polish is maintained after use, even when brought in contact with the most acid foods, and it only requires ordinary washing to cleanse. It is claimed that it retains a keen edge much like that of the best double-sheer steel, and, as the properties claimed are inherent in the steel and are not due to any treatment, knives can readily be sharpened on a "steel" or by using the ordinary cleaning machine or knifeboard. It is expected it will prove a great boon, especially to large users of cutlery, such as hotels, steamships, and restaurants. The price of this steel is about 26 cents per pound for ordinary sizes, which is about double the price of the usual steel for the same purpose. It also costs more to work up, so that the initial cost of articles made from this new discovery, it is estimated, will be about double the present cost, but it is considered that the saving of labor to the customer will more than cover the total cost of the cutlery in the first twelve months.



THE PLANT

STARTING A DYESTUFF INDUSTRY IN AMERICA.*

By DR. D. W. JAYNE.

There has been up to the present time no complete dyestuff industry in America, because hitherto there has been no economic reason for it. The producers of the crude materials had no excess and no other incentive, and the consumers of the dyes offered no inducement, their demands apparently being met satisfactorily by imports.

Until the advent of the by-product coke oven the production of coal tar increased but slowly, being entirely from plants producing coal gas. The first recovery oven in this country was established by the Semet-Solvay Co., about twenty years ago, though at that time by-product ovens abroad were an accepted fact. Besides this, the coal tar from gas plants has always been a factor abroad, especially in England, where as late as 1900 the gas tar alone was more than twice the oven tar of Germany, and seven times the combined production of both gas tar and oven tar in the United States. The small quantity produced in the United States in 1900 was due to the fact that so many plants here manufactured carburetted water gas, the tar from which is not included in these figures, that the tar from coal gas was and still is an exceedingly small item, and even in 1900 the number of recovery ovens was small—the rapid installation period coming after that date. Europe had many years' start of us, because they began to see the desirability, and perhaps the necessity, of providing outlets for the various coal-tar products, while we, up to the present time, have found no difficulty in disposing of those coal-tar products which might enter into the manufacture of dyes. As a nation we are not apt to plan far in advance, and the tar distiller did not give much thought to the dyestuffs under the existing conditions. The same condition held true in England, for England has no complete dye industry. Germany developed the coal-tar dye industry, using not only its own materials but many brought from England, until it has become one of the most complete industries in the world. The German dye manufacturers have also had every advantage of government aid in their development, and they present a united front to all competition. Here, the construction of by-product ovens has gone on until today about 25 per cent of the coke is produced in them, and still we have not produced a surplus of coal-tar products which could be used for dyes.

The products which are the basis for dyestuffs are benzol, naphthalene, and anthracene. Benzol and its homologues, toluol and xylol, occur in coal tar in small quantities. The chief source of benzol is the coke oven gases. The Semet-Solvay Co., besides installing the first recovery oven in the United States, also established the first benzol recovery plant in connection with their ovens. They now recover at all their plants, and are the sole producers of that which is available for refining today. Several other oven installations which sell gas to cities do remove the benzol from the fuel gas, but use it to enrich illuminating gas. The Semet-Solvay benzol is also used for enriching at some points, so that it is not all available for refining; but even so, there was a surplus of benzol less than two years ago, and the shortage today would be less marked had it not been for the depression in steel. Few consumers of benzol realize how fluctuations in steel affect supplies of benzol, but with the lessened demand for coke, less coal is coked, with consequent less by-products.

We are already independent of Europe—negligible quantities only of benzol have been imported during the past few years—the price levels here and abroad being approximately the same. The demand abroad is also heavy, due to the use of benzol for motor fuel, especially during the recent high price of gasoline.

Toluol is of more importance to the nation on account of its use in the explosive field than in the manufacture of dyestuffs, and an increase in supplies of benzol brings increased supplies of toluol, which will help the situation in the manufacture of explosives for our national defense.

An increase in benzol supplies will also make it possible to manufacture phenol synthetically. Phenol is today produced in the United States in less proportion to the country's consumption than any of the chemical bodies occurring naturally in coal tar. Our small production of phenol from our tar is primarily due to the small proportion of gas tar produced here, because the tar from coke ovens is deficient in true phenol. England has always been the great factor in phenol, simply because of its large production of tar from coal-gas plants.

Naphthalene, the second crude base, occurs in considerable quantities in coal tar. Until recent years the distillate from coal tar in the United States was taken off in only two portions, light oil and heavy oil;

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*Paper read before the New England Section of the Society of Chemical Industry and reprinted from the Journal of the Society.

the balance, pitch, remaining in the still, and the oils taken off to that point which left the correct grade of pitch. This means that pitch was the primary product sought for, and in fact remains so today. This is not to be wondered at, since coal tar yields on the average 70 per cent of pitch, used for roofing, paving, and water-proofing; and the American tar distiller began, and has remained, essentially a manufacturer of roofing and paving materials. This is quite different from conditions abroad, where practically their only use of pitch was for fuel purposes, until the advent of its use for road construction, which is of recent date. Credit is due to the American tar distillers for their efforts in building up a big business for pitch, this 70 per cent of all the tar—and for that reason we make a distinction between the coal-tar industry, which is an American development, and the coal-tar chemical industry, which is exemplified by the German production.

The heavy oil as produced here was sold just as produced, for creosoting timbers. In it was the naphthalene, and most of the tar acids, notably cresol, and with the ever-increasing demand for creosote oil, there was no reason for reducing the amounts available by removing naphthalene from it. Moreover, refined naphthalene has always come into this market at prices so low that it did not pay the tar distiller to remove and refine it. Certainly no more profit could be obtained by so doing than by its sale in the creosote oil, and large plant investment is required for the separation and refining of naphthalene.

Refined naphthalene has been produced here, however, for many years—practically since the beginning of tar distillation in this country, and our present production of it is nearly one third of the country's consumption. But it is nearly all used as a moth repellent—not any, as far as I know, having been used for the manufacture of any product entering into the dyestuff industry.

Conditions have altered somewhat in the past few years. Specifications have been drawn up for creosote oil which eliminate the lower boiling portion, and now an increasing quantity of middle oil is being separated and the naphthalene and tar acids recovered from it. More naphthalene can be recovered and refined, and no doubt will be, if a demand is assured, at a price commensurate with the added investment and cost of manufacture.

The separation of anthracene from the heavy oil is not now carried on in the United States. About thirty years ago there was a plant which separated small quantities of it for export, but this became no longer remunerative and was discontinued. It is now left in the creosote oil, but the quantity which could be obtained is a much less proportion of the tar than is recovered abroad, because all their tar is run to hard pitch, which is the grade used for fuel, that is, briquettes, while, as explained, we run, in the United States, for soft pitch. Thus, some of the high-boiling oils containing anthracene remain in the pitch. Some hard pitch is made here, however, and if a steady demand arose at a price commensurate with the investment and manufacturing cost, anthracene could be recovered probably in sufficient amounts for the needs of our dyestuffs.

It is well to remember that less than 10 per cent of tar consists of bodies which can be used for making dyestuffs, the balance being neutral hydrocarbon oils sold, even by Germany, for creosoting purposes only.

It is true we have an American coal-tar dyestuff industry. Nearly 20 per cent of our consumption is manufactured here, but until three years ago all the dyes made here were from imported intermediate products, or else were imported in a condition requiring only slight alteration to make them suitable for the trade.

In 1910 the Benzol Products Co. was formed. This company had as a central thought the fact that some day a very considerable amount of benzol would be recovered here, and that it was an opportune time to start operations in order to be ready to take advantage of those conditions when they arrived. Therefore the manufacture of nitrobenzol and aniline oil was undertaken. Thirty years ago the Schoellkopf plant, at Buffalo, had made aniline oil, and more recently the Barrett Manufacturing Co. had tried the manufacture of aniline and toluidine, and had a small plant which, however, had been used almost exclusively for toluidine, as toluol had been a drug on the market, its use for explosives, such as trinitrotoluol, not yet having been started. This previous experience had demonstrated the large part played by sulphuric and nitric acids in the manufacture of aniline oil, many more pounds of acid than of benzol being required for the manufacture of aniline oil; so that in the formation of the Benzol Products Co., the manufacturer of acids was represented. This same condition is evidenced in the plants in Germany, which have built themselves around and in connection with the manufacture of acids, alkalis, and heavy chemicals in general.

Since the Benzol Products Co. began it has perfected its manufacturing operations, and no doubt exists as to the quality of the product. The quantity, however, has been limited, primarily, because of the efforts of the foreign convention to nip its operations in the bud, and secondly, because of the shortage of benzol which was felt soon after it was in position to expand. Under these conditions it was deemed unnecessary to sacrifice any more benzol than was necessary to take care of those few buyers who had given visible evidence of their desire to encourage this American industry.

Here we see the attitude of the American consumers of dyestuffs. They were being supplied, at comparatively low prices, with a wide variety of dyes, continually improved as to fastness and new shades. They were buying direct from the representatives of the great German firms. Why buy one item such as aniline oil from us, especially as every offer as to price from us was bettered by their present suppliers? In fact, when a 10-per-cent duty on aniline oil and salt was secured in the recent tariff, the European Convention not only absorbed that duty, but made lower prices than before. There were several notable exceptions to this condition, and among them were several of the American dyestuff manufacturers. They no doubt realized more than the consumer how utterly dependent the United States was on foreign makers for our supplies of dyes. For them we continued to make aniline, but that was not enough encouragement to warrant any expansion, so that the outbreak of war found us still only manufacturing aniline oil, and not enough benzol in sight to warrant immediate steps to enlarge so that we could at least supply the country's demand on that one item.

The reason why we had not a better established and more complete dye industry years ago was essentially a matter of international economics. The United States had no surplus coal-tar products to dispose of, and no incentive in additional profits if it did offer refined products to dyemakers, as the intermediate products such as aniline oil, beta naphthol, etc., as well as the hydrocarbons themselves, such as naphthalene and anthracene, could be imported more cheaply than the tar distiller cared to attempt to make them. The manufacturers of dyes themselves had to meet very keen competition. In 1880 there was a sufficiently high duty on these dyestuffs and no duty at all on the intermediate products, so that at that time the dyestuff industry, based on imported intermediates, began to thrive; but in 1883, the specific portion of the duty on dyes was abolished, and a considerable duty assessed on the intermediate products, and as such intermediate products that far back could not be produced in this country, primarily on account of shortage of supplies at that time, many of the established factories closed down shortly after. There was again a period during which the intermediate products came in free, but the experience was evidently sufficient to prevent any resumption of this industry by the erection of any new plants, and the few factories who have stuck to their manufacture during the varying periods have made but little profit.

The possibilities and prospects primarily depend on the consumers of dyestuffs. Do they want an American dyestuff industry? Are they willing to help pay the price needed to establish it, and, if so, will they come forward and say so?

In the first place, there is sufficient coal tar produced in the United States today to give the necessary quantity of naphthalene and anthracene to supply our needs of dyes made from it. Plants to recover them could be erected as soon as plants to use them can be.

Benzol exists in by-product coke oven gases in quantities far exceeding the present needs of both the dyestuff requirements and the trades consuming benzol as a solvent. Efforts have been made, ever since a shortage was seen to be inevitable, to secure the erection of additional recovery plants, but little of the possible supplies can find their way to the dyestuff manufacturer and the other outlets are the controlling factor. However, there seems good reason to hope for partial relief during the next year, at least to an extent sufficient to enable the manufacturers of aniline oil to increase their production. It takes time to demonstrate to the owners of the ovens the advisability of investing in such a recovery plant, especially steel companies in times of depression as have existed, and it takes just as long to get the plant erected after the preliminaries are disposed of.

Any thought of prompt relief in the dyestuff situation is out of the question. We can have the whole complete industry for future use, if the consumers want it, but without a strong plea from the consumers, neither the tar distiller, the manufacturer of intermediates, nor the manufacturer of dyestuffs will risk the large amount of capital necessary.

To establish such an industry, to protect the country from a future shortage, requires one thing and one only—that is, adequate protection. Adequate protection means a higher duty on all dyes, and one-half the duty on dyes to be assessed on intermediates, and it also means protection against competitive methods which are aimed to crush and with which we have had experience. This latter protection can probably be best secured by a proper antidumping clause in our tariff.

Nothing else is necessary. We have the materials, we have the technical knowledge, we have the capital, we have sufficient unpatented dyes to make nearly everything actually needed, but we need protection.

The need of protection against unfair competition is obvious, but is the need for a higher duty equally so? Bearing in mind that we have no surplus products as yet, it must be made more profitable for the tar distiller to separate and refine the products needed than to leave them as they are today, to be sold in the oils. This means higher prices to the dye manufacturers and they, therefore, need some offset to enable them to sell their output in competition with the imported dyes. This immediately suggests the thought of the ultimate result on the price of materials if dyed with the higher priced dyes. I have been assured that the price of the dye itself is an absolutely negligible item in most costs of finished goods, and cannot possibly affect the price to consumers, and therefore puts the question directly before the users of the dyes. It is a question for them to answer whether they want an American dyestuff industry independent of Europe and are willing to pay the price to have it.

My personal opinion is that the additional price necessary to be paid by the users of dyes, in order to secure this industry, would not be a permanent increased cost. Tariff protection during the period of development only should be considered. Such an industry would be competing with one of the strongest and richest industries in the world, and competing only on products which are free to all as regards patent restrictions, while the German industry has made vast sums on its products during the life of the patents and continues to reap large profits on those items on which the patents have not yet expired. This means competing on those items which are now sold on close margin and having no exceedingly profitable items which have helped the Germans to earn their immense profits. Protection over a term of years to protect a growing industry has already been given by this government. The often cited example is the tinplate industry, which was given assurances of a continuing protection for at least ten years, and whose development was immediately begun with that promise. Today it is certainly able to hold its own with anyone. The same would be true of a dyestuff industry.

The initiative lies with the consumers of dyes. Will they make it plain to Congress that they want an American coal-tar dye industry?

DYESTUFF SITUATION IN THE UNITED STATES.*

Numerous American industries are closely dependent upon the use of dyestuff. To the great textile branches they are almost as essential as their supplies of vegetable or animal fibers. The same condition exists in the paint, varnish, and ink trades, the paper industry, the feather and leather trades, and a group of minor industries. Dependent upon the products of these industries are a host of other branches, all users of textiles. The old-time natural dyestuffs, such as indigo, madder, cochineal, orchil, fustic, and a score more, have no longer an extended use, with the exception of logwood, which still plays a valued auxiliary rôle. The same is the case with mineral colors, with some inconsiderable exceptions, such as Prussian blue in silks and iron buff in khaki.

Artificial dyestuffs, derived from coal-tar products, have displaced nearly all rivals, combining qualities of fastness, ease of application, brilliancy, variety of shades, etc., utterly unknown to the former generation of dyers.

The American consumption of artificial dyestuffs has attained an annual value of $15,000,000, and grows steadily.

It is supplied partly by a domestic production valued at about $3,000,000. This apparent domestic production is based chiefly upon the use of foreign materials—half-made or nearly completed color compounds. But a small portion is made from American crude coal-tar compounds.

The great bulk of the artificial dyestuff supply comes from Europe. The average imports are: From Germany, $7,850,000; Switzerland, $910,000; Great Britain and others, $370,000; total, $9,130,000.

Since August 1, 1914, in consequence of the outbreak of hostilities in Europe, this foreign supply has been interrupted and constantly threatened with nearly complete cessation. Until the present date, German makers have been able to supply a considerable proportion of the normal demands of their customers, but not entirely. Some important dyes are totally unobtainable. Prices have mounted from 25 to 50 per cent on such dyestuffs as can be delivered. The imports may cease any day through inability to make shipments, on account of maritime dangers, or what is more probable, through the military necessity of commandeering the available supply of the chief coal-tar crude material, benzol, for use as a motor fuel, or diverting the limited supply of nitric acid—the chief chemical used in color manufacture—to the manufacture of explosives.

The multitude of users of dyestuffs in the United States have been crippled in various ways, forced to change designs, or abandon certain products, or to revert to a temporary use of natural dyestuffs, with all the accessory readjustment and revolution in dyeing processes. On every hand there is difficulty in meeting contract specifications and in making definite plans and agreements for the future. The importation of dyewood has quickly increased. It is now four times as great as in normal times. Prices of these dyewoods have mounted. Fustic, for example, has doubled in price.

The four American establishments making artificial dyestuffs have done their best to meet the emergency by enlarging the ordinary output. They have been crippled by the difficulties or impossibility of securing half-manufactured materials from abroad or crude materials at home. Some large consumers of dyestuffs have erected emergency plants and make the colors they absolutely need, but at considerable cost.

In all this annoyance, loss, and uncertainty why do we not have an American coal-tar chemical industry, capable of meeting the nation's demands, self-contained and independent of foreign control, utilizing our native raw material?

A careful analysis of the situation shows that not only is the American supply and the limited American production of coal-tar dyestuffs completely dominated by the German industry, but that this is the case throughout the world. Even countries such as Great Britain and France, with ample supplies of crude material and highly developed industrial power, are in the same condition as the United States.

In 1913 the total consumption of artificial dyestuffs in the world had attained a value of over $92,000,000. Germany furnished 74 per cent of the entire amount and over one-half of the materials needed to make the remainder. The only country, in addition to Germany, manufacturing dyestuffs in any noteworthy manner for the world's markets is Switzerland. That country relies, however, for its crude and half-manufactured materials chiefly upon German sources. The dominance of Germany in the dyestuff production and commerce of the entire world is so marked, and inherently of such potential might, that it does not hesitate to make itself felt whenever and wherever an effort is made toward emancipation from its control. The methods used are those often associated with the working of great industrial corporations in various lands and now effectively checked by legal enactment in the United States. In the case of the German coal-tar chemical industry, the field is international and its operations are unchecked by law. Its influence has been felt at once in our own country when efforts to manufacture intermediate compounds or finished dyes threatened in any way the interests of the German production and trade.

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*Preliminary report submitted to the United States Senate by the Secretary of Commerce.

The coal-tar chemical industry includes not only the manufacture of dyestuffs, but a number of valuable medicinal preparations, and of various high explosives. It is based upon the use of crude compounds present to a small extent in the tar obtained in the destructive distillation of coal in gas works and coke ovens. These 10 crude compounds—benzol, carbolic acid, anthracene, etc.—are separated from some 145 other substances present in tar, by fractional distillation. This is the work of the tar distiller. From the 10 crudes, nearly 300 more complex compounds, none of them dyes, are produced by highly refined and complicated chemical and mechanical processes, involving in most cases a number of complete chemical transformations. These serve as the materials for the manufacture of about 920 dyestuffs now in current use.

In the case of Germany, the domestic supply of "crudes" is amply sufficient. The color factories make all of the 300 intermediates required for Germany's own industry and a large share of those used in the very restricted production of other lands.

The industry has been chiefly developed by the inventive power of German chemists, combined with a wealth of technical skill and keen business management, scarcely equaled in the history of any other branch of manufacture. The twenty-one German companies engaged in the dyestuff manufacture have a nominal capital of over $36,700,000, on which dividends average 22 per cent. Actual profits often reach 50 per cent. The great excesses have been devoted to new construction. It is the most remunerative industry in the empire, the one most solidly and formidably intrenched, the one of which the nation is most proud as showing the triumph of science applied to industrial purposes, and the one illustrating most strikingly the ability to win and maintain international supremacy in a given field.

In the United States the supply of coal tar is ample, sufficient to provide in abundance all of the crudes required for the manufacture of the dyestuffs consumed in the country. The amount of valuable by-products not yet recovered in our present coking plants amounts to $75,000,000 annually. With adequate provision to save all the benzol and tar liberated in American coke ovens, enough of the 10 crudes could be secured to more than cover the world's consumption in making artificial dyestuffs.

If a commercial demand is present, American tar works can quickly provide all of the crudes needed, practically as cheaply as in Europe. In the manufacture of intermediates the production is restricted to four or five compounds, and these cover about one-quarter of the needs of American color works.

Our manufacture of heavy chemicals is well developed, able to rapidly expand, and supply all needed chemicals for the production of intermediates and their transformation into finished dyes.

The four establishments devoted to the production of dyes supply nearly 100 different colors, largely, however, as already stated, by "assembling" nearly finished products of foreign origin. These American firms are bold and enterprising, commanding about $3,000,000 capital, evidently doing the best they can under existing conditions to build up a national industry.

Investigation shows that their advance, beyond certain limits, in the manufacture of either intermediate or finished dyes is persistently checked and prevented by the united action of German producers in underselling. The entire German color industry is so completely organized and accustomed to act as a unit in furthering the general interests, at home and abroad, that little success in facing their determined opposition has heretofore been obtained.

The present crisis has evoked deep interest on the part of all concerned—tar distillers, manufacturers of chemicals, manufacturers of dyestuffs, the many users of the same, and American economists in general—as to how the problem can be settled. There is no question but that our coke interests are ready to multiply their recovery plants for the production of benzol and tar, if a permanent market is assured. There is no question of the readiness of tar distillers to enlarge their plants for the production of an ample supply of the needed crudes if a continued demand is certain. American chemical works and American manufacturers of dyestuffs are ready to embark capital and experience in building up a distinctly American coal-tar chemical industry, using entirely American crudes and intermediates, provided there is adequate legislative prohibition against both "dumping" or unfair restraint of American trade by the arbitrary action of foreign monopoly permitted by foreign law and not as yet forbidden by our own. Foreign makers assert their ability to make at once over 90 per cent of the dyes now consumed in the United States, which are now patent free, and state that the remaining tenth will soon be freed from patent restriction.

There seems to be a consensus of opinion that any rapid development and evolution of the dyestuff branch, on a scale commensurate with the nation's needs, present and prospective, can be assured only on the basis of an effective law preventing that action toward control of our markets by a foreign monopoly which is now prohibited to a domestic monopoly. Some of the largest manufacturers have personally informed the department that what is needed is not a tariff change but laws placing a foreign monopoly on the same basis as an American one.

American economists feel that the present crisis offers the most favorable moment to decide upon a policy with regard to this one important industry, whether it is to be firmly rooted in American soil or whether the dependence upon a foreign source is to continue indefinitely. It is pointed out that each year elapsing increases in geometrical ratio the difficulties attendant upon any attempt to create a self-contained American dyestuff industry. Further, it is claimed that it is the only highly organized industry not yet brought on a broad and generous scale within the cycle of American economic activity.

In England and France the textile and other branches have insisted that the national industries must be permanently freed from dependence upon a foreign source for one of the vital needs of the most varied manufactures. Within a fortnight the group of French chemists intrusted with the problem claim that they have satisfactorily solved all difficulties in the way. During the same period the necessary steps have been taken in England, where the government has provided for the organization of a national company to create an independent dyestuff industry, contributing nearly $2,000,000 to its capital, and granting at the same time $500,000 for the requisite research laboratory.

COLLOIDAL GRAPHITE LUBRICATION.*

W. W. ACHESON, JR.

Recently, in a conversation with the author, the consulting engineer of the largest paper mill interests in Wisconsin remarked: "I have been connected with this company for thirty-seven years, rising from an operator to the position of general superintendent. In this present position, until the last year or two, I have thought that any employe capable of walking about with an oil can was good enough to oil machinery. I now see this is a very grave mistake, for oiling machinery requires intelligence and training. The idea of placing a cheap laborer in the position of caring for expensive machinery is a vital mistake." This point, though well known to men who have studied the subject, is very difficult to bring to the attention of the management of industries. To oil machinery properly it requires an intelligent man who *thinks* what he is doing, applies the *right* amount of the *right* oil at the *right* time and in the *right* way.

In order to adequately cover this subject it seems best to give illustrations of some conditions that are of daily occurrence and that seldom come to the attention of the heads of manufacturing plants. The following incident is typical:

Joe was a licensed engineer, looked upon as a capable man in his profession. He was placed in charge of a new power plant. After operating his engine for several weeks he found that the cylinder was not getting the lubrication necessary, and cutting was beginning to take place. The quality of the oil used was good; in fact, this oil was costing his "boss" 55 cts. per gallon. Joe would not go to the "boss" with his troubles, being afraid his job might be taken away from him. On the other side of the city a friend of Joe's was the chief operating engineer of a large central lighting plant, so Joe made excuses for a trip down town and went to consult with his friend, Fred. Now the first questions that Fred asked, after Joe had told his troubles were:

"Are you using dry or saturated steam?

"What is the steam pressure carried in your boiler?

"What is the piston speed of your engine?

"What is the nature of the boiler compound you are using?

"Is your engine working to capacity or half load?"

When Joe had answered these and several other questions, and, by the way, he had to return to his plant to get the answer to most of them, then Fred said:

"Your trouble is that you are using too *good* an oil. Get a cheap, heavy, black oil, about the cheapest thing you can find and use it one drop every two complete revolutions of the engine. Do this and you will get the results you desire."

This is simply one illustration of the necessity of selecting a lubricant suitable to the requirements, for to attempt to use the same oils for every class of lubrication in a plant is folly and shows ignorance of one's work. A selection of the proper oil for each class of machinery to be lubricated is necessary if one wants to produce shop efficiency and economy. A high speed bearing will require a different lubricant than that required by one moving slowly and doing heavy duty.

Not so long ago the author was in a sugar mill watching seven men attempting to operate a "hog" for the grinding of cane. Now they had been endeavoring for better than two weeks to make this machine run. They had tried every lubricant obtainable and even had piped running water to each of the journals, and yet the best they could get was about 20 minutes running, when the journals would become heated to the melting point. They removed the babbitt and repoured the bearings with new metal and still it ran hot. In watching these men endeavoring to make this machine run it seemed that its speed was excessive. By means of an indicator it was quickly determined that the speed was 218 rev. per min. above the running time recommended by the manufacturer. In this case a heavy, roughly constructed machine was being run at a higher speed than its journals could stand. Upon changing the driver this hog ran very well and no more heated journals were had. Nevertheless, the company had lost several hundred dollars in experimentation.

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*From The Wisconsin Engineer.

Aside from selecting an oil, it is necessary to have the working conditions as nearly correct as possible. Neither oils, nor greases, nor colloidal graphite nor anything else in the way of lubricants will correct a mechanical difficulty. But, when your working conditions are as they should be, then the addition of colloidal graphite to the ordinary lubricants will reduce friction by more than 20 per cent.

Colloidal graphite was invented by Dr. E. G. Acheson, who in 1897, first produced artificial graphite on a commercial scale. While carrying on experiments with carborundum in an electric furnace, he noticed that when the substance was brought to a temperature far beyond that of its production, decomposition occurred and the silicon portion of the carborundum dissipated as volatile matter, while the carbon proportion remained as pure graphite. It now requires two plants which have a total equipment of about 9,000 hp. to supply the demand for graphite. This is being shipped to all parts of the world, the consumption in 1913 being 16,000,000 lbs.

Graphite is manufactured in electric furnaces which are under perfect control and which reach a temperature of 7,500° F., so that all substances except carbon are volatilized. The remaining carbon is thus extremely pure and is entirely converted into graphite. In fact, entire furnace loads have proven to contain more than 99.90 per cent pure graphite carbon. The small amount of non-graphitic material consists of condensed mineral gases collected during the cooling of the furnace. Since the power is at all times under absolute control the entire process is flexible so that any quality of graphite desired can be produced by varying the raw material used, the method of running the furnace, and the amount of power expended.

After this chemically pure graphite is produced in the electric furnace it is then reduced by a process of disintegration and passed through a sieve having 40,000 meshes to the square inch. The resulting powder is much finer than the finest flour, but not reduced to a condition where it can be employed in connection with oils as a lubricant. In order to secure a still finer subdivision this disintegrated graphite is subjected to a treatment called "deflocculation." This consists in a mastication of the disintegrated graphite with a water solution of tannin, the amount of tannin being 6 per cent by weight of the amount of graphite being treated The tannin enters into and explodes the individual particles of the disintegrated graphite to a condition approximately 1,000 times finer than their original state. To give a clearer idea we will say that disintegrated graphite is of such fineness that it takes 338 particles to cover the distance of 1 inch, when these particles are placed side by side; after the tannin treatment the resulting deflocculated graphite is of such fineness that it requires 338,704 particles to cover the distance of 1 inch. This reduction in lineal dimensions means a reduction of cubical volume corresponding to the cube of 1,000, or the ratio of the size of the individual particles is as one drop of water is to 264 barrels of water.

Graphite in this condition of fineness is on the market under the trade name of "Oildag"; O-I-L plus deflocculated Acheson graphite, and is being used in every class of lubrication.

Oil containing colloidal graphite (deflocculated graphite is now being aptly termed colloidal and liquid graphite) constitutes a most dependable form of lubricant. When introduced into a bearing the graphite particles, being infinitesimal, penetrate the pores of the metal. These particles accumulate until the surfaces in contact are completely amalgamated with a thin veneer which has been termed a graphoid surface. This film, unlike that of oil, is free from intrinsic friction and exceedingly stable in its construction, being capable of withstanding far greater pressure than any form of hydrocarbon regardless of its viscosity.

The graphoid surface not only greatly reduces friction but practically eliminates wear. So lubric is the nature of this graphite film that upon its establishment oil consumption may be considerably reduced. It has been recorded that one-sixteenth less oil is necessary when colloidal graphite has been used. If the oil supply of a bearing is either accidentally discontinued or completely consumed, the original graphoid surface alone will hold up as a lubricant for a long time, preventing a hot bearing.

It has been found, after many exhaustive tests, that 0.35 per cent of colloidal graphite properly diffused in oil is sufficient.

Colloidal graphite in gas engine lubrication possesses many advantages over plain oil. The formation of carbon deposits in cylinders results from the inability of the piston rings to effect a thorough wiping back of the lubricating oil, so that a portion remains in the cylinder and is decomposed. This source of trouble usually ceases with the use of colloidal graphite. The minute particles of the graphite enter the interstices of the metal and form a soft, unctuous film that is not attainable by any mechanical operation.

With the establishment of this film or amalgamation of graphite upon the cylinders, and upon the face and sides of the rings, there is effected a perfect fit between the walls of the cylinders and the rings, due largely to the freer action of the rings in their grooves. This fit produces or causes a clean wiping back of the excess oil after each splash, so there remains no oil to decompose and produce carbon. What carbon deposits there may be formed will be found to be of a nature similar to damp lamp black and may be wiped off clean. There will be an entire absence of the hard burned carbon that causes cylinder troubles.

Dr. C. H. Benjamin, now dean of Purdue University, while he was with the Case School of Applied Science of Cleveland, Ohio, made a number of tests with colloidal graphite. One of his trials was made on a journal having a pressure of 125 lbs. per square inch, and running at 445 rev. per min. This test was made using the same oil and same rate of feed for two runs, all conditions identical, excepting that colloidal graphite was added to the oil in one run. A lower coefficient of friction was very noticeable with the addition of the graphite. After two hours' lubrication with the oil, the feed was shut off while the bearing was permitted to run and within ten minutes the lubrication from the oil failed, producing an abrupt rise in friction, which necessitated stopping the run. By the addition of colloidal graphite to the same oil for a period of two hours before shutting off the feed, there resulted an almost perfect lubrication over the time of one hour and twenty minutes, thus showing that the graphite is dependable as a lubricant when the oil feed is cut off.

Another interesting experiment was conducted by Dr. Chas. F. Mabery, of the Case School of Applied Science. He also shut off the oil feed after two hours, and let the journal run. In just nineteen minutes the plain oil lubrication failed absolutely, while the same oil carrying colloidal graphite gave a perfect lubrication for four hours after the feed had been cut off. In this test Dr. Mabery used a pressure of 200 lbs. per square inch and 450 rev. per min.

There remains one more point worthy of mention. Colloidal graphite, being molecular, refuses to associate with an acid or alkaline oil. Some of the oil refineries use the acid process to precipitate the coloring matter or heavy carbons that are present in oils, and then fail to remove all this acid. Every oil to be a good lubricant should be neutral. The presence of acids, in any appreciable quantities, in oil, detracts from their lubricating value. A very simple and very positive test for the presence of acid in oil is to take a 2-oz. bottle of the oil and thoroughly mix say 30 drops of "Oildag" with this amount and allow the mixture to stand undisturbed for two to five days. If the oil is neutral there will be no signs of precipitating of the colloidal graphite. Should there be a decided precipitation then the oil is acid and therefore is not the best to be desired for lubrication. If graphite is not carried in diffusion, but caused to settle out of the oil, then it ceases to be colloidal graphite. A colloid, being a solid in suspension but not in solution, cannot be precipitated.

A number of German textile concerns were able to declare a higher dividend for 1914 than for 1913, while a number have been obliged to reduce it. A comparison of dividends of 34 of the most important German textile firms shows an average dividend of 5.65 per cent for 1914 and of 8.44 per cent for 1913, being an average decrease of 2.79 per cent.

FERTILIZER MATERIALS IN THE IMPORT TRADE.*

The increasing extent to which American farmers must rely upon domestic fertilizers as soil foods is suggested by figures issued by the Department of Commerce through the Bureau of Foreign and Domestic Commerce, which show a decrease last year of 240,000 tons in the receipts of potash salts as compared with 1912 or 1913. The imports of that group of potash salts most largely used for fertilizer purposes amounted in the calendar year 1914 to 702,800 long tons, compared with approximately 942,000 tons in each of the two years immediately preceding.

Muriate of potash, sulphate of potash, kainit, and manure salts are the classes of potash usually designated as fertilizers, their value as soil food being dependent upon their content of K_2O. The muriate usually yields about 50 per cent of K_2O; the sulphate, 48 per cent; kainit, 12½ per cent; and manure salts, 20 per cent. On this basis the year's supply of imported K_2O was 176,354 tons, against 228,757 tons in 1913 and 226,722 tons in 1912.

Of guano the imports increased from 19,100 tons in 1913 to 25,600 tons in 1914, and those of ammonia sulphate from 58,300 tons to 74,100 tons. Calcium cyanamid, or lime nitrogen, is not reported monthly, but for the fiscal year ending June 30, 1914, the imports were 30,000 tons, or double the amount for the preceding year. Only a slight change occurred in imports of bone dust and ash, the total increasing from 34,600 tons in the calendar year 1913 to 36,000 tons last year. Of basic slag the imports in 1914 were approximately 10,000 tons, a decrease of 33 per cent from those of the preceding year. Crude phosphates, of which the United States is the world's chief producer, show importations to the amount of 24,000 tons, while apatite, a phosphate of unusual purity, decreased in quantity of imports from 3,000 tons in 1913 to less than 100 tons last year.

The decrease in imports of potash salts extends to other groups used in the chemical and other manufacturing industries. Carbonate of potash fell from 21½ million pounds in 1913 to 16 million pounds last year; nitrate of potash, from 10 million to 2¼ million pounds; caustic potash, from 8½ million to 7¼ million pounds; and other salts, except the cyanamid, from 6 million to 5 million pounds. Cyanamid of potash slightly increased, from 1 million to about 1¾ million pounds.

The aggregate value of potash salts and fertilizer materials imported into the United States in the calendar year 1914 was 38½ million dollars, as compared with 47 million dollars in the preceding year. Nitrate of soda decreased in value of imports from 21½ million to 15¼ million dollars, and sulphate of ammonia increased from 4 million to 4½ million dollars.

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*From Daily Commerce Report.

A summarization of imported potash salts and other fertilizers, in tons, for the last two years follows:

Articles.	1913.	1914.
Kainit	465,900	329,600
Muriate of potash	213,800	168,500
Sulphate of potash	39,500	36,300
Manure salts	223,300	168,400
Nitrate of soda	625,900	543,700
Sulphate of ammonia	58,300	74,100
Bone dust and ash	34,600	36,000
Guano	19,100	25,600
Apatite[1]	3,000	100
Calcium cyanamid[1]	15,000	30,000
Phosphates, crude[1]	24,000	24,000
Basic slag[1]	15,000	10,000
Other substances used as manure[1]	115,000	197,000

[1] Fiscal year figures.

The year's purchases of the foregoing classifications had an aggregate value of $37,117,000, as compared with $45,069,000 in 1913.

NEW ADHESIVE FROM SULPHITE WASTE LIQUOR.*

Frederick H. Patch, of Manchester, Va., has taken out a patent on an adhesive and the process of making it from waste sulphite liquor. Describing it fully in the specifications, he says:

In the present process of preparing or manufacturing an adhesive compound I use the waste or spent liquor from the paper or pulp mills or any waste liquor or prepared solution containing resinous matters, sulphurous acid, and bases such as potash, soda, magnesia, or lime. I also use the waste or spent liquor from soda pulp mills, and any waste or spent liquor containing resinous, dextrin, and starch matters.

My invention when carried out to its fullest extent is a process or method of treatment which consists in, first, making the spent liquor alkaline by means of a base, then concentrating it to a suitable density, then adding flour, clay, sawdust, and saponified animal, vegetable or mineral oils or fats, or in preparing the concentrated liquor in such a way that the animal, vegetable, or mineral oils or fat when added is saponified in the composition, thus forming an adhesive liquid compound of commercial value, or by the evaporation of this compound to full dryness and pulverizing the residue, a dry compound.

In carrying out the invention I concentrate the waste or spent sulphite or soda liquor, etc., by evaporation to a thickness or density: for example, a specific gravity of 1.3 to 1.4, sufficient to keep a soapy or saponified substance in suspension. In making the improved adhesive compound from these above mentioned spent liquors or by-products, I follow two different methods: to add saponified substances to the concentrated liquors or to prepare the concentrated liquors in such a way that the animal, vegetable, or mineral oils or fats when added to the preparation are saponified therein.

To procure the soapy or saponified substance I take animal, vegetable, or mineral oils or fats and combine therewith a sufficient quantity of hydrates or carbonates of potassium and sodium, any compound or composition containing potassium or sodium in excess, and also resin. Any soapy or saponified substance, thus procured, is then mixed with the concentrated liquor in proper quantity as desirable.

If desired to make a compound containing flour-clay or flour and clay, both these materials are mixed with the concentrated liquor before the soapy substance is added. Sawdust when used may be added to the mixture before or after the addition of the soapy substance, as most convenient. The flour may be mixed to the concentrated liquor direct or dissolved or mixed in water, and if both flour and clay are used these are mixed together dry or with water before mixed with the concentrated liquor. Flour, clay, and sawdust are added in a quantity as required for different purposes and according to circumstances.

To prepare the concentrated spent sulphite liquor and the by-product such as may contain saccharine substance so as to saponify oils and fats when added, I add to said liquors hydrates or carbonates of potassium and sodium or any compound or composition containing potassium or sodium hydrate or carbonate in excess, for example, the concentrated spent liquor from soda pulp mills in a quantity sufficient for the saponification of the animal, vegetable, or mineral oil or fat that is then added to the composition. Flour-clay or flour and clay and also sawdust, if used, are mixed with the concentrated liquor before the alkaline matter is added in the same way, as above described. The process of manufacturing may be carried on with or without the aid of artificial heat, as convenient or desirable, and the liquor may be further concentrated after the addition of the soapy substance, or the oil, or fats, if necessary. In manufacturing the dry compound or compounds, I take either of the above-said concentrated spent liquors or by-product, or any compound made from them, as above described, evaporate it to absolute dryness and then pulverize the residue.

The adhesive liquid and dry compounds are intended chiefly for use as binders for sand in the foundry practice in making up cores and molds and in the manufacturing of briquets from coal, charcoal, sawdust, all kinds of ores, etc., and the above-described variations in the compositions are principally for the purpose of adapting them for use with different kinds or characters of sand, etc. As is well known, some sands contain in themselves clay substance (loam) while others are practically free from all clay substance. In one instance, the clay in the sand itself will obviate the necessity of adding clay to the composition to secure the binding qualities desired, while in the other instance the addition of clay is desirable. By the term "loam" I mean the natural substance commonly known by that name.

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*From Paper.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

50th Meeting of American Chemical Society.

The American Chemical Society will hold its fiftieth meeting in New Orleans, on Wednesday, March 31st, to Saturday, April 3rd, inclusive.

The chief feature of this meeting promises to be the symposium of the Industrial Division, which is to be held on Thursday, April 1st. The symposium will be opened by an address by A. D. Little, presenting some of the vast opportunities open to the South in the chemical industry. The symposium will be closed by a public address to the people of New Orleans, given by Dr. Hesse, on Thursday evening. Some thirty papers have been promised in all for this symposium, many of them by some of our best known chemists, as J. B. F. Herreshoff, W. P. Mason, and W. D. Horne, Daniel Wesson and others.

The general program of the meeting is given below:

Wednesday, March 31.

9:00 a. m.—The whole day, up to the time of leaving for the afternoon excursion, will be given up to visiting points in the city which are interesting historically or chemically.

4:30 p. m.—Excursion on the Mississippi River, to be followed by a smoker on the steamer. The presence of the ladies at the smoker is especially desired.

9:00 (?) p. m.—Meeting of the council at the Grunewald Hotel to be held immediately on returning to New Orleans.

Thursday, April 1.

9:30 a. m.—General meeting, industrial symposium, Tulane University.

12:30 p. m.—Luncheon at the Tulane refectory, tendered by the University. Inspection of the University.

2:00 p. m.—Continuation of industrial symposium.

2:30 p. m.—Personally conducted walk through the Vieux Carré for visiting ladies.

7:45 p. m.—Public address by Bernard C. Hesse on "The Chemists' Contribution to the Industrial Development of the United States—A Record of Achievement."

9:00 p. m.—Reception at the Round Table Club, tendered by the Club.

Friday, April 2.

9:00 a. m.—Meetings of divisions at Grunewald Hotel.

2:00 p. m.—Meetings of divisions at Grunewald Hotel.

2:00 p. m.—Motor ride for visiting ladies.

2:00 p. m.—Visit to the New Orleans Water Purification plant by the Water, Sewage and Sanitation Section.

8:30 p. m.—Subscription dinner. Grunewald Hotel.

Saturday, April 3,

8:30 a. m.—Excursion to the salt mines at Avery's Island. (To be undertaken only if at least seventy-five persons signify their intention to participate.)

Paper Lint for Dressing Wounds.

European army surgeons, according to *Paper*, are using paper lint as a dressing for wounds. It is preferably made from cotton rag and soda poplar, but the bleached and well beaten fibers of spruce reduced by the sulphite process should prove equally serviceable. The cellulose should be free from resin which interferes with its absorbent property, an important factor in a substitute for lint and cotton in the dressing of wounds. The lint or wadding is made on a Flying Dutchman by running the pulp in an extremely thin sheet or lap, one drying machine only being used. The dried sheet is peeled off the cylinder by means of a doctor and reeled up between rollers to form a sheet of lint or wadding of any desired thickness. It follows from the process of manufacture, which demands free bleaching by either electrolytic soda or chlorine and copious washing, that paper lint can be depended upon as being perfectly aseptic.

Air Excess in Boiler Practice.

We have received the following letter from Mr. W. D. Brown, Chief Chemist, Duquesne Works of the Carnegie Steel Co.:

In regard to the article on air excess in boiler furnace practice in your January issue allow me to say a few words.

Several of the methods are based on the amount of carbon, hydrogen, etc., burnt, some on the carbon in flue gas. These are variables depending upon whether all the carbon is burnt and none entering the ashes and on the chemical analysis of the coal. Kent's and Gill's formulae have the advantage that the ratio of carbon to hydrogen in the fuel has no effect on the formulae; the percentage of nitrogen in the coal alone having a bearing and that is negligible. But Gill uses round figures and neither takes into consideration the carbon monoxide in the gas. The excess air should be that over amount necessary to combine with any carbon monoxide present. For instance, a flue gas containing .5 per cent O_2 and 1 per cent CO should be considered as containing no excess oxygen since, if carbon monoxide were burnt, the apparent excess would disappear.

The method in this journal, January 1910, page 15, gives a formulae:

$$\text{Excess air} = \frac{1.89\,(2\,O_2 - CO)}{N_2 - 1.89(2\,O_2 - CO)}$$

or

$$\frac{3.78\,(O_2 - \tfrac{1}{2}\,CO)}{N_2 - 3.28\,(O_2 - \tfrac{1}{2}\,O)}$$

By this formulæ the excess air in the gas given in your January, 1915, issue contains 140.5 per cent air in excess of that required. If one-half the carbon monoxide be subtracted from the oxygen to obtain the excess oxygen this new figure will show the same results, 140.5 per cent, by Kent's formulae.

Soya Bean Situation in North Manchuria.

Deputy Consul William Morton, Harbin, China, reports that the soya bean crop of North Manchuria in 1914 was estimated to be 15 per cent larger than that of the preceding year. The total exports of beans from North Manchuria from Nov. 1, 1913, to Nov. 1, 1914, amounted to 415,000 tons, of which about 33,000 tons were exported via the Sungari and Amur Rivers, 100,000 tons to Dalny and Japan, and the remainder to England, Germany, the Netherlands, and Denmark.

Shortly after the outbreak of war in Europe the transportation of Russian troops over the Chinese Eastern and Trans-Siberian Railways began, and so interfered with the shipment of commercial freight that not more than one-third of the bean cargoes have reached Vladivostok, the remainder being stored at the various stations of the Chinese Eastern Railway. Now that the transportation of troops has ended it is expected that there will soon be enough freight cars for carrying the beans to Vladivostok.

There are three small modern bean-oil mills in North Manchuria, one of which belongs to a Japanese and the other two to Chinese. The full capacity of these mills is about six short tons of oil daily. Besides these three mills, a large modern mill (oil) has been built by the Anglo-Chinese Trading Co. at Harbin, but it is not working yet, as its machinery is not complete. There are numerous small Chinese oil mills operated either by hand or by horse power scattered throughout the towns and villages of North Manchuria, but no statistics are available as to the total output from these mills.

Baskets are used for transporting oil from the surrounding country to Harbin, but wooden boxes and tins packed in wooden boxes are used for containing oil for export abroad. One wooden box contains about 252 pounds of oil and one tin contains about 36 pounds of oil, two tins being packed in one box. The tins and boxes are of local manufacture. No empty tins were imported into North Manchuria in 1914.

Turkish Supply of Gum Tragacanth.

Owing to the scarcity of labor due to military levies the gathering of most of this year's yield of Asia Minor gum tragacanth was prevented. The local stock remaining from last year does not exceed 30 tons. There has been little demand this year from European buyers, but some small shipments have been made to the United States. Prices are abnormally low, but increased freight rates bring them to almost the usual level. Good natural gum sells for 38 cts. per pound c. i. f. New York. The white variety is slightly dearer.

Russian Dyemaking Scheme.

A Petrograd report states that the scheme for establishing coal-tar color works in Russia has not been abandoned. A project is under discussion which is said to have the support of the leading dyestuff consumers in the country, and it is thought to have very good prospects of success. The proposed capital of the concern is $5,000,000, the whole of which is to be provided by home consumers. It is stated that the seven largest calico-printing companies in Russia—including the Baranoff Co., the well known printers and Turkey-red dyers, and the E. Zündel Co., Moscow—representing an aggregate capital of over $25,000,000, have together promised about $2,200,000 toward the new undertaking. It is proposed to erect tar-distilling plants and manufacture right from the raw product.

POSITION WANTED as assistant chemist. Completed the I. C. S. General Chemistry Course and the manufacture of sulphur and hydrochloric acid. Married. Have a responsible position in another line of work; desire a change. Box 6, Chemical Engineer, Chicago, Ill.

The Chemical Engineer
PUBLISHED MONTHLY
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COLOR PHOTOGRAPHY: ITS PRINCIPLES AND PRESENT APPLICATIONS.

By **ARTHUR C. NICOLET.**

Written for THE CHEMICAL ENGINEER.

Although color photography is rather more complicated, it depends on much the same principles as does monochromatic (ordinary) photography, and can be more easily explained on the basis of a general knowledge of the principles and manipulations of that kind of work. Hence a general review of these principles and applications will not be out of place in this paper.

The sensitized plate (or film) on which the negative is made consists of a sheet of glass (or celluloid) covered with a coating of gelatine containing very fine particles (less than one eighth-hundred of a millimeter (00125 mm.) in diameter) of silver bromide (silver chloride and silver iodide are used to a slight extent). This plate is placed in a camera and "exposed," that is the image, in light, of the object to be photographed, is allowed to fall on it. The light starts the reduction of the translucent, almost transparent, bromide to black, opaque, finely divided, metallic silver. The plate is then "developed" by being placed in a chemical bath which continues the action of the light, intensifying the several portions of the image in proportion to the quantity of light which has struck them. After the image has reached the desired blackness, the plate is placed in the "fixing bath" which dissolves the unaffected silver bromide, thus preventing any future action of light. These manipulations give a picture in black and various shades of gray in which the "color" is reversed, the brightest portions of the original being black and the shadows being transparent. If, however, instead of placing the plate in the fixing bath, one bleaches it with certain chemicals, exposes it to strong light, and redevelops it, one "reverses" the image, getting a picture in various shades of gray, of the object photographed, in which the light portions of the object to be photographed are shown light and the dark portions dark.

This picture, however, does not show the shades as the eye sees them, either in color or in relative intensity. The untreated plate is more sensitive to blue and ultra-violet (which does not affect the eye) than it is to the other colors. It is somewhat sensitive to yellows, rather more so to greens, but is almost unaffected by red. Because of this difference in the relative effects of the several colors, the color values, as stated, are not true to nature. A bright red dress which will "catch" the eye, will appear in the picture as of practically the same shade as will a black suit. The yellows and greens, which are among the most plentiful and the brightest colors in nature, appear dark, while the blues appear almost white. This condition may be remedied, as far as color values are concerned, in either of two ways; by speeding up the reds, yellows, and greens, or by retarding the blues and the violets. In practice both of these means are employed. Certain dyes applied to the gelatine emulsion will do the first and a sheet of orange tinted glass (a different tint is required for each kind of orthochromatic plate) in front of the lens will do the second. We now have a plate which portrays fairly faithfully in black and grays the shades of the original object.

The results, however, are still rather disappointing at times. You see a beautiful autumn landscape, snap it, develop it and so forth, and behold, you have a black and white picture of ——, —— a few acres of real estate. Again, you see a snow picture; there you think, there is no color in nature, so you take it. It also is dead, without the blues of the shadows and the sky, and the brown tinge of the limbs of the trees. And similarly you are disappointed on most of the subjects you essay (no matter how expertly you carry out the work). Therefore, the processes of color photography have been devised.

The underlying physical facts making color photography possible are two. At the distance of fourteen inches (the distance for ordinary vision) the eye cannot "resolve" or see as two, two points separated by less than two tenths of a millimeter (.2 mm.). Second, all colors as seen by the eye may be built up of three primary colors, which, for transmitted light, are red, blue and green (for pigments they are red, blue, and yellow). Now, if I have a number of very fine particles of these three colors within a circle two-tenths of a millimeter in diameter, I will not see the various colors, but will get the impression of *one* color, whose shade depends on the proportion of each of the three primary colors present. Since a transparent red particle is red because it transmits light of that color and absorbs light of any other color, a person could, by placing a sheet of transparent red substance in front of his plate during the exposure, get a picture showing only the red in the original subject. If now we should take a similar one with a green screen and another with a blue screen, and after development, reversal, and fixation should dye each one to the proper intensity, and should superimpose the three in such a manner that they exactly coincide, we would get a picture of the original subject, which when viewed by transmitted light would appear in its original colors. This process, however, would be too complicated for amateur use, so instead of taking three pictures on three plates, screens of fine particles of transparent green, red and blue, mixed thoroughly in proper proportions are made and the orthochromatic plate covered with a single layer of particles. Now, if a picture be taken on this plate, with the particles toward the lens, developed, reversed, and fixed, leaving the particles undisturbed, the resulting effect will be the same as that in the three-plate process. The three pictures, however, will all be on one plate. One third of the plate will be completely red (in various intensities), one third will be completely blue, and the remainder will be completely green. These portions, however, will be so intermingled that the effect received on viewing is not an agglomeration of spots of the primary colors, but of a blended color which is very similar to the color of the original object.

The various methods of accomplishing color photography may be divided into three classes: those using a single plate with a single screen combining the three colors, those using a plate for each color and superimposing them, on one another, and those depending on diffraction. The third of these is probably totally impracticable and as it is interesting only from a theoretical standpoint, I will omit a discussion of it from this paper. The first and second, however, find commercial application and will find it more and more. The second, though, is used only in moving pictures and will therefore not be discussed until the last portion of this paper. The first method may be conveniently subdivided into: processes in which the color screen is integral with the plate, and processes in which it is separate from the plate. The Lumiére plate is, I believe, the only plate of the first subdivision. Of the second the McDonough-Powery and Paget processes will be described.

A Lumiére autochromatic plate is made as follows. A clean piece of glass is covered with a very thin coat of gelatine. Very fine starch granules, less than one one-hundred twenty-five thousandths of a millimeter in diameter, are prepared, one-third dyed each of the three primary colors, and the whole thoroughly mixed. These are applied to the gelatine surface in a layer just one particle deep (precisely how this is done is, I understand, a trade secret) and pressure applied. This pressure makes an almost solid sheet of particles, but a few small interstices are left which are filled with fine carbon, or other opaque substance. This layer is then covered with a varnish and on top of the varnish with an ordinary orthochromatic emulsion. The plate is put into the camera with the glass side towards the lens, and the picture taken through the glass and starch particles. This process has the disadvantage of being non-reproducible, that is, duplicates can not be made of the original plate. However, the Lumiére plates have been on the market since 1907 and are proving a success.

The two processes of the second subdivision (namely those in which the screen is separate from the plate) are reproducible. They have many points in common, differing in fact, only in the kind of color screen used. The McDonough-Powery uses a screen with very fine lines of alternate red, blue, and green and the Paget one with very fine squares of the same colors (made by having lines running in two directions, at right angles to each other). A further description of the screens may, however, be more properly given after the description of the process and the method of applying it. The orthochromatic plate (made on especially thin glass) is mounted in the plate holder with the emulsion outward, and a screen placed against it with the color towards the plate (the holder should have a spring behind the plate to hold the plate and screen in close contact). The plate is then "exposed," removed from the plate holder, and it alone placed in the developer. It is not reversed but left as a negative. After this has been washed and dried, a print of it is made on a sensitized plate similar to a lantern slide, but of rather better quality. The "print" is developed, fixed, and washed (this part of the process does not in any way differ from that followed in the making of ordinary lantern slides). The "print" is then dried, and either the screen used in taking (which has not been in any way impaired) or an exactly similar screen is superimposed upon it and shifted until the colors of the screen are over the corresponding portions of the print (determined by the effect given upon looking through them. The screen is best adjusted when the color effect is best). These are then bound together in a way similar to that in which a lantern slide is bound to its cover glass. Obviously, as many of these prints may be made as desired. The only limit is the number of similar screens available, and in either process all screens made are interchangeable.

The McDonough-Powery screen is made photographically. Gelatine, which has been treated with potassium dichromate, becomes insoluble upon action of light, so a thin glass plate is coated with a thin coat of bichromated gelatine, dried, and exposed under a finely ruled glass plate which is ruled with parallel, opaque lines which are just twice as wide as the clear spaces between them; all of the opaque lines being of exactly the same width. This exposed plate is then placed in water to dissolve off the unaffected gelatine, and the whole immersed in a bath of blue dye, mordanted, and dried. Another coat of gelatine is then put on and the screen again exposed with the ruled plate moved over the width of one clean space. It is again immersed in water, then in red dye, then in a mordant, and again dried. It is again coated with gelatine, exposed with its back toward the light and treated as before, using a green dye. Obviously, all screens made from the same plate, at the same temperature, are interchangeable. I do not know how the Paget screen is made, but I believe it to be mechanically ruled. The McDonough-Powery process was on the market for a time, but has been withdrawn until it can be "speeded up" sufficiently for moving pictures (Edison Company). The Paget process is on the market at present.

The chief, if not the only important drawback to color photography in its present development, is that the retarding effect of the color screens (that in front of the lens and the red, blue, and green one) and of the dye used in increasing the red sensitiveness, increases the time of exposure necessary to from 25 to 100 times that for the untreated plate. This, of course, eliminates color photography for snap-shots.

Methods of color photography for moving pictures, however, have been and are used, but they either give only approximately the colors of nature, or use more than one film. Two systems have been extensively tried, the Graumont and the Kinemacolor. Of these the Kinemacolor has been the most extensively shown in this country, New York being the only place in America where the Graumont pictures have been shown. Neither of these follows the practices for ordinary color photography.

The Kinemacolor depends on the fact that two (or more) images received by the eye in less than about one-tenth of a second appear as one. In taking the pictures the exposures follow one another more rapidly than in monochromatic motion picture photography. One exposure is made through a bluish green screen, the next through a reddish green, the next through the first screen, and so on. The reason for using only two instead of three colors is that the retarding effect of the screen is sufficient, under present conditions, to make the taking of more than two pictures in the tenth of a second available, an impossibility. The colors must necessarily be only approximate, but they appear fairly natural. Rapidly moving objects, however, show in distorted colors, caused by motion between images.

The Graumont process uses three different colors, but requires more expensive taking and projecting apparatus. In it, three pictures are taken with lenses side by side, in the three primary colors, and projected through lenses, from one arc light with suitable reflectors.

The McDonough-Powery process is now (or at least was until the fire at Orange, N. J.) being worked on at the Edison plant, in an attempt to speed up the working to a point where rapidly moving objects may be portrayed. It is said that they can now take a picture of a dog jumping and "stop" him.

BARITE OF THE APPALACHIAN STATES.*

By THOMAS L. WATSON and J. SHARSHALL GRASTY.

(Concluded from March issue.)

Tennessee[24]—In Tennessee barite is found in many localities, but the more important deposits occur in the eastern part of the state and are grouped into two districts: (1) The French Broad district, which includes parts of Cocke and Sevier counties on the North Carolina line, and (2) the Sweetwater district, centered about the town of Sweetwater and including parts of Loudon, McMinn, and Monroe counties. Barite has been reported mined also in Bradley, Jefferson, Smith, and Washington counties; and it occurs as a gangue mineral in a lead mine near Haysborough, Davidson County, and as veins in dolomite 12 miles from Greeneville, Green County.

The French Broad district includes parts of Cocke and Sevier counties, located on the North Carolina line in the mountainous region of the state, south and a little east of Knoxville. The barite occurs in veins from 1 to 6 ft. in thickness, which closely resemble those of Madison County, North Carolina, but owing to lack of transportation the deposits have only been worked to a limited extent. Thus far, the principal developments have been near Wolf Creek in Cocke County. The deposits are reported to contain ample reserves of the mineral, and they carry practically none of the impurities associated with the residual deposits of barite in the Sweetwater district.

The Sweetwater district is the largest and at present the only important producer of barite in Tennessee. It includes parts of Loudon, McMinn, and Monroe counties, centered within a radius of 20 miles about the town of Sweetwater on the Knoxville division of the Southern Railway, 42 miles southwest of Knoxville. There has been extensive development and a considerable production of barite in the past. The principal shipping point is Sweetwater, where is located the mill of Gilman & Son for the treatment of the mineral, but other shipping points located on the same line of railway include Philadelphia, Reagan, and Niota. Most of the barite is graded and shipped to the Eastern markets. Several companies operate in the district, but the mineral is handled almost entirely by farmers who work between crops.

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*From Transactions of American Institute of Mining Engineers.

[24] Fay, A. H.: Barytes in Tennessee, Engineering and Mining Journal, vol. lxxxvii, No. 2, p. 137 (Jan. 9, 1909).

Grasty, J. S.: The Barite Deposits of Tennessee, The Tradesman, vol. lxix, pp. 34 to 38 (1913).

Henegar, H. B.: Barite Deposits in the Sweetwater, Tennessee, District, The Resources of Tennessee, State Geological Survey, vol. ii, pp. 424 to 429 (1912).

Herzig, C. S.: Tennessee Barytes, The Mineral Industry, vol. x, p. 58 (1901).

Judd, E. K.: The Barytes Industry of the South, Engineering and Mining Journal, vol. lxxxiii, No. 16, pp. 751 to 753 (April 20, 1907).

Watson, Thomas L.: Fluorite and Barite in Tennessee, Trans., xxxvii, 890 (1906).

Weller, C. A.: Barytes Mines of the Commercial Mining and Milling Company (Tennessee), Engineering and Mining Journal, vol. lxxxiii, No. 18, p. 851 (May 4, 1907).

The barite deposits of the Sweetwater district are of the residual type, occurring as nodules and boulders of varying sizes and shapes in the clays derived from the weathering of folded and faulted rocks which range in age from Cambrian to Ordovician. (See map, Fig. 7.) The principal workable deposits, however, are found in the residual clays derived from the Knox dolomite. In places the mantle of residual clay, in which are assembled the nodules and boulders of barite, is 60 ft. and more in thickness, but usually averages from 10 to 15 ft. Only in one or two workings have the excavations extended down to the hard rock limestone.

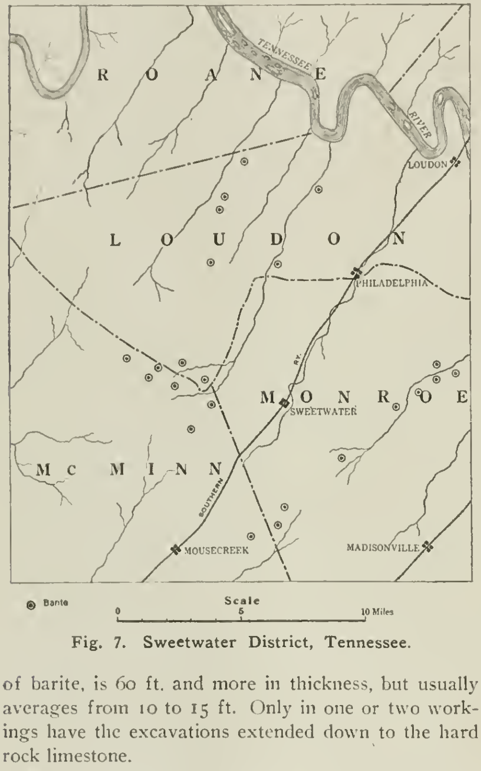

Fig. 7. Sweetwater District, Tennessee.

A large percentage of the barite mined in the district is coated with limonite, which on account of the slight difference in specific gravity of the two minerals is difficult to remove even by jigging. Freeing of the barite from the iron oxide before grinding is necessary, as it is very difficult to bleach the mineral thoroughly afterward. Besides iron oxide the barite is intimately associated with chert.

An analysis of a sample of barite taken from the Roy property gave: BaSO$_4$, 97.56; Fe$_2$O$_3$, 0.42; SiO$_2$, 0.41 per cent. A less favorable sample from the Terry property gave on analysis: BaSO$_4$, 94.12; Fe$_2$O$_3$, 0.70, SiO$_2$, 2.45 per cent.

Mining of barite in the Sweetwater district is carried on entirely by open-pit work with pick, shovel, wheelbarrow, and wagons. In some cases the clay encountered is indurated, and because of its toughness it is necessary to break it down by an explosive. This, however, is the exception, although an explosive might be used at times to advantage in even the less-hardened clays.

Virginia[25]—In Virginia, barite has been mined since 1845. In the Piedmont region the mineral has been mined in Bedford, Campbell, Louisa, Pittsylvania, and Prince William counties; and in the Valley region in Montgomery, Russell, Smyth, and Tazewell counties. The barite deposits occur in three unlike areas: (1) In the red sandstone-shale series of the Triassic, (2) in the old crystalline metamorphic pre-Cambrian and Cambrian rocks, especially in some of the crystalline limestone areas, and (3) in the Valley region of folded and faulted Cambrian and Ordovician limestones. Areas (1) and (2) compose the Piedmont province, which extends eastward from the Blue Ridge to the fall-line or the western margin of the Coastal Plain sediments. The map, Fig. 8, shows the distribution of worked barite areas in Virginia.

Thus far the Prince William County deposit near Catlett, in the northern part of the state, is the only one in the Triassic rocks that has been worked to any extent. It has been idle since 1903. The barite occurs as a filling or cement of crushed and fractured impure limestones and red shales. The widest of the barite-filled fractures is 4 to 8 ft. The barite is of good white quality, finely to coarsely crystalline massive, and is largely free from most of the common impurities. The mineral was mined by shafts and open cuts, the greatest depth reached being 108 ft.

The principally worked barite deposits of Bedford, Campbell, and Pittsylvania counties, in the south central part of the state, are centered about Evington, Campbell County, and Toshes and Sandy Level, Pittsylvania County, as shown on map, Fig. 9. The area is one of greatly altered crystalline rocks formed from old sedimentary and igneous rocks. The barite occurs as irregular lense-like bodies or pockets replacing crystalline limestone associated with micaceous and quartzose schists, and as nodules and lumps in the residual clays, which are limonitic or manganiferous and have been used in the manufacture of natural mineral pigments. Besides calcite and silicate minerals of the inclosing rocks, the associated minerals are galena, pyrite, and less sphalerite and chalcopyrite, in the unaltered deposits; and manganese oxide and iron oxide in the residual deposits. These impurities are often developed only sparingly and are not noticeable in the best grades of the barite. Fig. 10, an ideal section in the Bennett mine, Pittsylvania County, illustrates the mode of occurrence of the mineral in Campbell and Pittsylvania counties.

A sample of the black manganiferous clay collected from the Bennett mine, Pittsylvania County, by the senior writer and analyzed by W. B. Ellett, gave:

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[25] Watson, Thomas L.: Geology of the Virginia Barite Deposits, Trans., xxxviii, 710 to 733 (1907).
———: The Geology of the Virginia Barite Deposits, The Tradesman, Mar. 20, 1913, pp. 38 to 41, Mar. 27, 1913, pp. 31 to 33.
Campbell, M. R.: Bristol, Virginia-Tennessee, Folio, No. 59, U. S. Geological Survey (1899).

	Per cent.
Insoluble residue	14.20
Alumina	4.96
Ferric oxide	32.40
Manganous oxide	19.49
Lime	2.06
Magnesia	trace
Barium oxide	trace
Copper	trace

The composition of the associated crystalline limestones is shown in the analyses below, made by W. B. Ellett on samples collected by the senior writer.

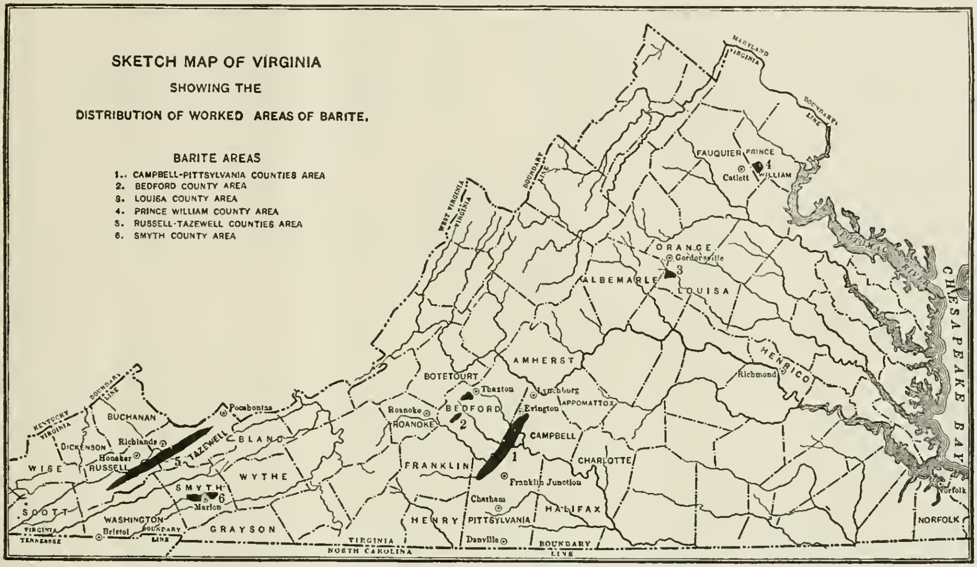

Fig. 8.—Sketch Map of Virginia Showing Barite Areas.

	1 Per cent.	2 Per cent.	3 Per cent.
Insoluble matter	1.66	0.87	1.10
Alumina Iron oxide	0.24	0.30	0.96
Barium sulphate	0.62	0.65	1.62
Calcium carbonate	89.36	93.33	91.07
Magnesium carbonate	6.61	2.82	3.73
Copper sulphide	trace	trace	0.36

1 and 2. White crystalline limestone from the Hewitt mine, Campbell County.

3. White and pink crystalline limestone from the Ramsay mine, Pittsylvania County.

The barite is won chiefly by shafts and drifts, and open cuts and pits. The greatest depth reached is 160 ft., at the Hewitt mine in Campbell County.

Barite is found in association with similar rocks in other counties of the Piedmont province, but has not been mined to any considerable extent. In the western part of Bedford County, about 3 miles northwest of Thaxton, barite has been mined from a fracture-filled deposit in a coarse granite. The mineral is crystalline, white to blue-gray in color, and in places contains much disseminated galena in small grains and occasional sphalerite. In Louisa County coarsely crystallized barite has been mined 3 miles south of east from Lindsay. It occurs in veins in schists and is remarkably free from impurities other than the usual discoloration from red iron oxide and some quartz. Several promising deposits of barite in the vicinity of Bealeton, Culpeper County, have been opened but no shipments have been made.

In the Valley region of southwest Virginia, in Tazewell, Wythe, Russell, and Smyth counties, barite occurs in the Cambrian and Ordovician limestones and their residual clays. The mineral occurs in the limestone as replacements and veins associated with sphalerite, galena, pyrite, and some fluorite. In Tazewell and Russell counties the common associates are limonite, chert, and calcite, with some siderite, and occasional fluorite.

Barite has been extensively mined near Marion, Smyth County, and extensive deposits are found in Russell and Tazewell counties, chiefly along the southern slope of Kent Ridge and its prolongation northeast and southwest, along the valley of Clinch River, extending from near North Tazewell to near Lebanon, a distance of more than 30 miles. The mineral has been mined at several points along this belt, the principal mines being near North Tazewell, 3 miles south of Richlands, 3 miles from Honaker on the Clinch River, and at the southwestern end of the belt near Lebanon. The barite is found in the upper part of the Knox dolomtie. Figs. 11, 12, and 13 show the structural relations of the Knox dolomite and the adjacent rocks on the northwest and southeast, near Sword Creek and Richlands, in Tazewell County.

The barite occurs as lumps of varying shapes and sizes assembled in the residual clays of the limestone, and in pocket form and vein-like bodies filling spaces in the limestone, and in part as replacements of the limestone. The mineral is crystalline, of good white quality, and in most places is practically free from impurities. The greatest depth reached in mining is 103 ft. at the mines of the Pittsburgh Baryta & Milling Corporation on the northeast end of the belt. Most of the mining done has been for the barite nodules in the residual clays, won from shallow open pits and cuts. Some hard-rock mining in the limestone has been done in places.

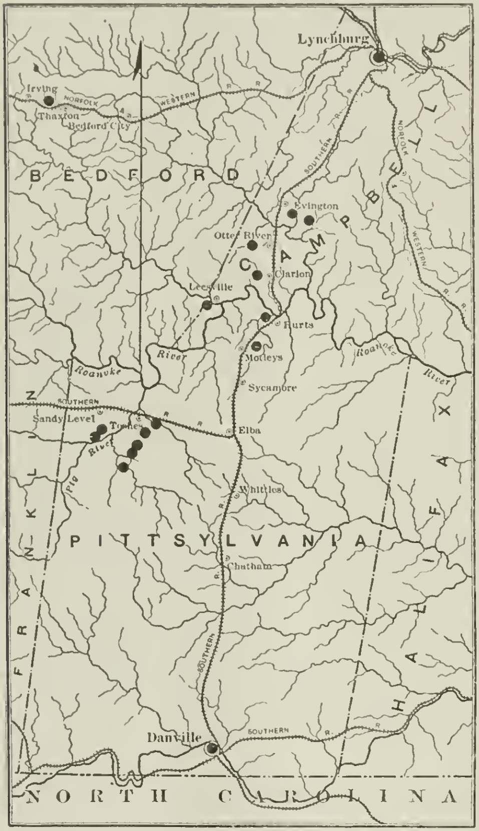

Fig. 9. Barite Deposits of Bedford-Campbell-Pittsylvania Counties Area, Virginia.

MINING METHODS.

Mining of barite in the Appalachian States is chiefly surface work, with no really deep mining in any part of the region. Thus far the mineral has been won chiefly by open cuts, shallow shafts, and pits, which rarely exceed 40 ft. in depth, usually much less. This method of winning the mineral is especially applicable to the occurrence of barite in loose nodular masses of different sizes and shapes irregularly assembled in the residual clays.

In some districts, especially the Piedmont region of Virginia and central Kentucky, shafts ranging from 50 to 400 ft. in depth have been sunk. In Piedmont, Virginia, the barite is won by vertical timbered shafts and drifts which follow the mineral bodies, and the greatest depth yet reached in barite mining is less than 200 ft. In the central Kentucky region a depth of about 400 ft. has been reached but the shafts have been chiefly for prospecting. Tunneling has been practiced to some extent in this region in the high cliffs bordering the Kentucky River, where the veins are exposed for a vertical distance of 300 to 500 ft.

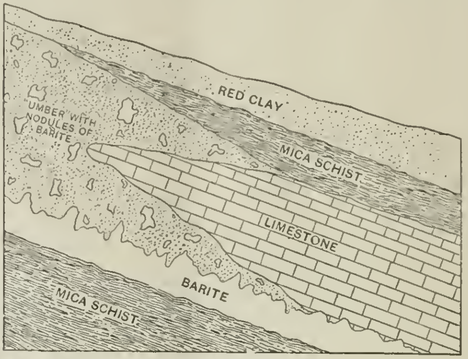

Fig. 10. Ideal Section in Bennett, Barytes Mine, Pittsylvania County, Virginia.

Blasting is necessary for breaking down the barite in the vein and limestone replacement occurrences of the mineral.

DEVELOPMENT AND TRADE CONDITIONS.

The majority of the deposits of barite are so scattered and many of them so small that the problems connected with their operation are those of handling the mineral and getting it to market rather than of mining. However, there is room for much improvement in the methods of mining barite, as is evidenced by the large percentage of loss in the working of deposits that occur in residual clays. This loss, which in some cases amounts to as much as 30 per cent, is from the small lumps and grains recoverable by washing and jigging but too small for cutting and sorting by hand. A large number of the deposits are located at a distance from railway transportation, as well as being far removed from mills, and while this is a disadvantage that obtains in many instances, still many deposits occur which would be worked were not the freight rate the main deterrent. On the other hand, the problem that confronts the manufacturer at times is the difficulty of accumulating sufficient barite to keep the mill running continuously. The reason why the raw material is not always available is due to the fact that the barite producer lacks, because of decreased profits, the same incentive that actuates the manufacturer. Moreover, the foreign producer has found that he can deliver his product to the larger city markets, like New York, Philadelphia, Baltimore, and others, cheaper than the domestic producer can deliver by rail.

Where barite occurs in residual clays the best way to handle it with a sufficient quantity of ore in sight would be with a steam shovel and suitable washers, but since few, if any, deposits are large enough to warrant the installation of such a plant and water is not everywhere plentiful the slower methods of mining, cobbing, and rocking must be employed. However, by employing energetic methods resulting in cheaper mining and the winning of a large percentage of the mineral that goes now to the dump heap in shape of small lumps and grains, the barite operators could increase considerably their present margin of profit, and thus operate profitably a large number of the deposits now idle.

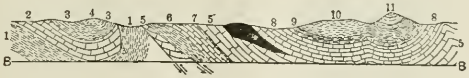

Fig. 11. Relation of Barite (A) and Rocks.

METHODS OF PREPARATION.

The preliminary treatment of barite for the market will vary according to the character of the mineral. In some localities the barite contains little or no impurities, in others the amount and character of the impurities vary greatly. The minerals associated with barite vary locally, but, broadly speaking, they vary in accordance with the mode of occurrence, whether residuary, or as veins and replacements. The more commonly occurring minerals are iron oxide, manganese oxide, limestone including calcite, and silica in the form of both quartz and chert, in the residual deposits; and the metallic sulphides, especially galena and sphalerite, fluorite, and calcite, in the vein and replacement deposits.

For the removal of impurities from the merchantable barite the principal steps in the preparation for market include hand cobbing, sorting or grading, washing, and crushing. For ground barite, bleaching, drying, and grinding are necessary. Such associated minerals as galena, quartz, calcite, and limonite, can be removed largely by hand cobbing during mining, but if these are inclosed in the barite, crushing and washing may often serve to cleanse it. Jigging is often found to be advantageous, especially if the iron oxide is in the form of scales or crusts, and it may be successfully employed for removing impurities of light weight, such as chert, limestone, etc. After the mineral has been hand cobbed at the mine into the several grades, it is shipped to the mills for further cleansing by crushing and washing to remove as much of the impurities as possible.

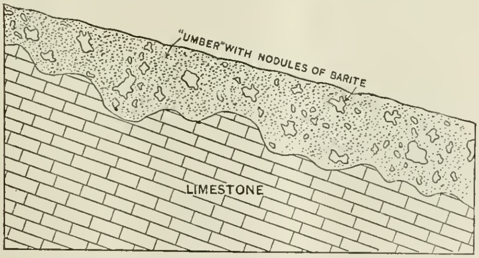

Fig. 12. Shows Structural Relations of Barite and Rocks; Barite Is Shown in Black.

Much of the barite mined in the Appalachian States is won by opencut work in residual clays derived from limestones; hence, the barite nodules are usually more or less stained with iron oxide and coated with clay. A method often practiced for freeing the mineral of these, especially the clay, is to assemble the nodules and lumps of the mineral in piles exposed to the weather, after which it is better prepared for hand cobbing and is given such additional cleansing as necessary prior to shipping to the mills. In some cases washing the mineral in log washers is practiced, but this is not always feasible, since an ample water supply may not be available, and also loss of the fine material is likely to result from this treatment.

In some localities in the Appalachian States the washers installed have been crude and the management poor, hence poor results have been obtained. When feasible, however, log washing and jigging would yield a product vastly superior to that produced by sun-drying methods. Washing will not entirely cleanse the ore in all cases, especially when the nodules and lumps are coated with a heavy crust of iron oxide, as is often the case with the residual deposits, but it will appreciably reduce the iron content and correspondingly increase the price demanded.

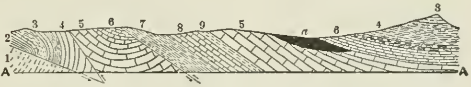

Fig. 13. Principal Mode of Occurrence of Barite in Russell and Tazewell Counties, Virginia.

Milling—Crude barite is treated by a number of different processes preparatory to a considerable range of uses. The equipment of the mill will depend upon whether the object be to prepare and market a ground and purified product, or to carry the treatment further by employing the comminuted material in the manufacture of compounds into which barium enters as an essential ingredient.

The barite as mined may be treated by either the wet or the dry process, the object in both cases being to reduce it to an impalpable powder and eliminate impurities, the two most difficult and deleterious being calcium carbonate and iron oxide. The former reacts injuriously with the acids of paints and the latter is objectionable because of its color.

In case the wet process is employed, suitable crushing, pulverizing, and jigging machinery is installed and the barite is kept in contact with water from the beginning to the completion of the treatment. When it is sought, however, to prepare the ground and purified product by the so-called dry method, the dry material is first passed through crushers and then cleansed as far as possible by water in log washers. The log washer, however, only partly eliminates such impurities as galena, sphalerite, iron oxides, calcite, fluorite, etc., hence it becomes necessary to bleach the material in an acid solution.

An outline of the complete process as followed by a thoroughly equipped mill has been described by Burchard as follows:[26]

> The crude material is ground in slip mills having granite grinders and granite bases. Water is fed into these mills and the ground material is floated over the top of the tanks, after which it is pumped into funnel-shaped separators. The contents of the separators are agitated by flowing water and the coarser rejected material is drawn off at the bottom of the funnel and returns to the slip mills, while the finer material floats off at the top of the separators. This material next descends to settling tanks, and after forming a sludge is drawn off into bleaching tanks. The bleaching tanks are built of concrete lined with refractory tile. Bleaching is accomplished by the addition of measured weights of sulphuric acid to the sludge and the agitation of the mass to secure thorough mixture. The acid reacts on the iron oxide and lime present, forming ferrous sulphate and calcium sulphate. The iron salt being soluble and the calcium salt partially soluble, besides having a lower specific gravity than the pure barytes, these substances, together with the excess of sulphuric acid, are removable in the further washing process to which the material is subjected. For this next washing the material is pumped into washers which employ the float-separation process. Next, the bleached barytes passes to settling tanks, after which it is dried by being spread thinly on the surface of a rotating hot drum. From the hot drum the dried material falls or is brushed off and carried to Williams mills, where it is pulverized, screened, and finally sacked by machine. The essential difference between this process and the others mentioned above is in the fact that the material is first reduced to a fine condition before bleaching, thereby bringing the sulphuric acid intimately into contact with all portions of the barytes.

Bleaching—Nearly all crude barite requires bleaching before the requisite degree of whiteness can be secured for the finished product. In order to free barite from iron stain, bleaching with sulphuric acid is necessary. The mineral is first crushed and washed, when it is ready for bleaching. The degree of fineness to which the mineral is crushed will depend upon the amount and character of iron present. In the Appalachian States, the barite is usually crushed to a size varying from that of a pea to ½ in., according to the amount of iron oxide, and whether it is in the form of scales or crusts, or as a stain. Jigging is necessary in some cases to remove the iron stain. Higgins[27] has described the bleaching process as follows:

> The crushed mineral is bleached in circular wooden tanks, lined with sheet lead. Each tank is provided with a 2-in. lead pipe, coiled in the bottom, closed at the end, and provided with small perforations, 7 in. apart. Steam escaping from the perforations agitates and heats the bleaching solution. This is sulphuric acid diluted to about 20 or 30° B. The mineral is charged into the tanks to a depth of about 3 ft., after which the acid solution is run in and steam is turned on. The time required to bleach the mineral varies from 6 to 80 hours, depending on the iron content. It is the usual practice to leave the steam on continuously, although good results may be obtained by cutting it off for half an hour at intervals of one hour.
>
> A tank 4.5 ft. high and 8 ft. in diameter is a convenient size for bleaching, containing, when charged to a depth of 3.5 ft., approximately 14 tons. It should be made of stout, well-seasoned wood, preferably cypress, should be well braced on the outside, and lined on the inside with heavy sheet lead. Connections should be provided so that either steam or water may be supplied through the perforations in the lead pipes. These perforations are best located at an angle of 45° off the vertical rather than directly on top, in order to prevent clogging of the pipes with fines.
>
> One of the greatest items of expense in the process is the steam for heating and agitating the bath. This may be greatly reduced by use of an ordinary injector, using a mixture of air and steam instead of steam alone. The amount of air can easily be regulated, so that the acid will not be too much cooled. The temperature may be kept at 200° F.; better agitation will result; the acid will suffer less dilution from condensing steam; and the steam consumption will be reduced one-half.

Should manganese dioxide be present in the barite it is not removed by the bleaching process. It becomes necessary then to grind the barite containing manganese oxide to a paste on a 40-mesh screen, and mix it in the proper proportion with sodium nitrate, salt, and sulphuric acid. The mixture is heated in a specially constructed furnace, which converts the iron and manganese into soluble chlorides that are readily removed by washing, the barite being collected in a series of settling tanks (unually three in number).

After bleaching, the barite is reduced to the size of fine sand by rolls and then to an impalpable powder by buhrstones, after which it is ready to be packed for shipment.

Drying—In drying bleached barite regard should be had for an even temperature, in order that none be sent to the mill imperfectly dried, otherwise it may "sweat" before going to the buhrs, which will yield a finished product that is off color. If mechanical conveyors are used for delivering the barite, care should be taken that the material does not come in contact with oil.

Grinding—For use in the paint and rubber trade the barite must be finely ground. This is accomplished almost entirely by buhrs, since no other method of grinding yet tried has proved so satisfactory in reducing the material to the required degree of fineness.

BARIUM COMPOUNDS.

Barium enters as a principal constituent into a number of artificial compounds, which have a wide range of uses. Some of the more important compounds include barium oxide, barium chloride, barium carbonate, lithopone or lithophone, and blanc fixe. These are briefly described below in the order named.

Barium Oxide—This compound is prepared according to the Bradley and Jacobs process by treating a mixture of barite and carbon in the electric furnace.

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[26] Burchard, E. F.: Mineral Resources, U. S. Geological Survey, pt. ii, p. 687 (1907).

[27] Higgins, Edwin: The Mineral Industry, vol. xiii, p. 34 (1904).

The following reactions which occur simultaneously are reported:

$$4BaSO_4 + 4C = BaS + 4CO + 3BaSO_4$$
$$3BaSO_4 + BaS = 4BaO + 4SO_3$$

Barium hydrate, used chiefly in the beet-sugar industry, may be obtained from the resultant mixture by treating it with hot water. In France, barium dioxide is used in the production of hydrogen dioxide, which finds an extensive use as an antiseptic and bleaching agent.

Barium Chloride.—As practiced by a Southern plant, this compound is prepared by heating in an 80-ft. rotary cement kiln a mixture of barite and coal, which after reduction yields barium sulphide and barium carbonate. The resulting mixture is leached with water, which removes the barium sulphide, and the residue treated with hydrochloric acid. The sulphide solution is treated with hydrochloric acid, filtered, purified, and evaporated to the point of crystallization.

Barium chloride has extensive use in the color industry and in the manufacture of wall paper. The fused chloride is used to a limited extent in tempering tool steel.

Barium carbonate (artificial), imported as witherite, is used to neutralize the soluble sulphates in those clays employed for the manufacture of terra cotta, to a limited extent in the manufacture of glass, and as a chemical reagent.

The Seurre process[28] for the manufacture of barium carbonate from barite consists in heating to the fusion point with constant stirring equal parts of pulverized barite and calcium chloride with 5 or 6 per cent of powdered charcoal in a crucible or furnace. The mass when leached in water yields a solution of barium chloride and an insoluble residue of calcium sulphate. Barium carbonate is precipitated from the filtered chloride solution by the addition of a 50 per cent solution of ammonium chloride may be treated with chalk, and the ammonium carbonate and calcium chloride returned to the process.

Lithopone.—Originally lithopone consisted of a simple mixture of barium sulphate and zinc sulphide, but later this was improved upon and the two were obtained as a double precipitate. At present the product may consist of barium sulphate with either zinc sulphide or zinc oxide or both. In the trade lithopone has been known under different names, such as Charlton White, Orr's White, Griffith's White, Becton White, etc. The best grades of lithopone are white, but inferior grades may be some shade of gray, brown, or yellow, due to the presence of such impurities as carbon, iron, etc.

The method usually employed in the precipitation of lithopone consists in mixing solutions of barium sulphide and zinc sulphate in the proportion of 51 parts of the former to 49 parts of the latter, which results in the precipitation of barium sulphate and zinc sulphide. The barium sulphide is prepared by heating a mixture of crude barite (four parts by weight) and fine coal (one part) to bright red heat in a reducing atmosphere. "In Germany lithophone is made largely from zinc sulphate obtained directly from ore at the works in the lower Harz, but in the United States the zinc sulphate is chiefly obtained by dissolving scrap zinc, or zinkiferous by-products, in sulphuric acid. At one works scrap brass is the source of the zinc employed."[29]

Blanc Fixe is chemically pure barium sulphate, and is precipitated from a solution of barium sulphide either by sulphuric acid or by salt cake. When salt cake is used sodium sulphide is formed, for which there is a limited market. The artificial barium sulphate ("blanc fixe") is pure and free from grit, and is employed chiefly in the manufacture of the finer grades of white paint, oil cloth, and paper. Large quantities of the product used in the United States are imported from Germany.

Until within the past few years this product was confined to the imported lithopone, chiefly from England and Germany, but an important home industry has now been established, and in 1908 at least nine firms in the United States were manufacturing lithopone.

MANUFACTURERS OF BARIUM PRODUCTS.

A table giving the names and addresses of the consumers of crude barite in the United States was published in *The Mineral Industry,* vols. xvii to xx (see bibliography at end of this paper for page references).

Uses.—Much the greater part of the production of barite is consumed as an inert pigment in the manufacture of mixed paints, the ground mineral being used both in its natural and in its artificial forms for this purpose. For this use the mineral must be finely ground, washed, bleached with acid, and floated. As a pigment, barite is stable in the presence of acids, alkalies, and gases, since it undergoes no chemical action and is inert as to color. Its crystalline nature renders it unsatisfactory as a pigment if used alone, and only moderate percentages should be used in mixed paints in order to secure the best results. Barite is considered a good base upon which to precipitate other colors, and it is used to dilute other pigments which tend to destroy the oil. Moreover, it gives "tooth"[30] to a coat of paint, so that a second or third coat will adhere.

According to Gardner and Heckel, probably the largest amount of barite is used in the production of the artificial pigment lithopone, which consists of 70 parts of barium sulphate and 30 parts of zinc sulphide. They say:[31]

> An enormous tonnage of this pigment is at the present

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[28] The Mineral Industry, vol. xiv, p. 45 (1905).

[29] The Mineral Industry, vol. xvi, p. 95 (1907).

[30] "'Tooth' is an expression used to describe the brushing action of a paint, which indicates that the paint is being taken up by the wood or other surface to which it is applied." Bulletin No. 93, Sept., 1914, p. 2355.

[31] Gardner, H. A., and Heckel, G. B.: Barytes as a Paint Pigment, Bulletin No. 93, Sept., 1914, p. 2353.

> time being used in the manufacture of interior flat wall paints of the oil type, such paints having almost entirely supplanted the use of corroded white lead which was at one time used for interior painting. The more dense nature, lower price and sanitary value of lithopone were responsible for this change. Lithopone is, moreover, used to a large extent in the manufacture of oil cloth, shade cloth and linoleum. Its whiteness makes it of particular value for this purpose. Barium sulphate is also used of itself in admixture with other pigments in the manufacture of prepared paints. The chemically precipitated form of barium sulphate, which is generally called *blanc fixe,* is also used for this purpose.

These writers conclude that there should be no technical objection to the use of barite in paints. They say:[32]

> The only question is an economic one, and involves two considerations: The first is that barytes and other inert pigments shall not be sold except under their true names and shall not be used as adulterants, using that term in the sense given it by the American Society for Testing Materials, as follows: "Adulterant—A substance partially substituted for another." The other consideration is that the amount of barytes shall be such that it will not impair the opacity of the paint under the conditions of application, which implies that three coats shall effectively hide the underlying surface to which it is applied.

The uses of some of the more important barium salts have already been stated. Barium is also used in the manufacture of glass, especially in rolled glass, hollow ware, crystal and table glass, and in such special glasses as the Jena phosphate crown glass, which is reported to contain 28 per cent BaO. Other uses of barite are in the manufacture of rubber, wall paper, asbestos cement, tanning leather, refining sugar, pottery glazes, enameling iron and oil cloth, poker chips, coating canvas ham sacks, and in the preparation of fertilizers, boiler compounds, insecticides, hydrogen peroxide, and artificial driftwood salts.

BIBLIOGRAPHY.

The subjoined list is not a complete bibliography of barite, but it includes the most important recent contributions to the literature. Other references not included in the bibliography are cited under individual states.

Alzugaray, Baxeres de: Composition, Distribution, and Production of Barytes, *Mining and Engineering World,* vol. xxxvii, No. 1, p. 17 (July 6, 1912).

Andrée, K.: Ueber ein bemerkenswertes Vorkommen von Schwerspat auf dem Rosenhofe bei Clausthal, *Zeitschrift für praktische Geologie,* vol. xvi, p. 281 (July, 1908.)

Bryant, F. C.: Barytes Industry of Cole County, Mo., *Engineering and Mining Journal,* vol. xcv, No. 6, p. 317 (Feb. 8, 1913).

Burchard, E. F.: A Barite Deposit Near Wrangell, Alaska, *Bulletin No.* 592, *U. S. Geological Survey,* pp. 109 to 117 (1914).

Canadian Mining Journal: Nova Scotia barite, vol. xxxiii, No. 18, pp. 661, 662 (Sept. 15, 1912); No. 19, p. 678 (Oct. 1, 1912).

Catlett, Charles: Barite Associated with Iron Ore in Pinar del Rio Province, Cuba, *Trans.* xxxviii, 358, 359 (1907).

Engineering and Mining Journal: Barium Salts, vol. xcvi, No. 20, p. 1015 (May 20, 1911).

Fay, A. H.: Barytes in Tennessee, *Engineering and Mining Journal,* vol. lxxxvii, No. 2, p. 137 (Jan. 9, 1909).

Fohs, F. Julius: Barytes Deposits of Kentucky, *Kentucky Geological Survey,* ser. iv, vol. i, pt. 1, pp. 441 to 588 (1913).

Frazier, Schuyler: Barytes, Occurrence and Methods of Preparation, *Chemical Engineer,* vol. xiii, No. 2, pp. 43 to 46 (Feb., 1911).

Gardner, H. A., and Heckel, G. B.: Barytes as a Pigment, *Bulletin No.* 93, Sept., 1914, pp. 2353 to 2355.

Grasty, J. S.: Barite Deposits of Kentucky, *The Tradesman,* July 3, 1913, pp. 33, 34.

——— Barite Deposits of Alabama, *The Tradesman,* July 17, 1913, pp. 35, 36.

Hayes, C. W., and Phalen, W. C.: A Commercial Occurrence of Barite near Cartersville, Ga., *Bulletin No.* 340, *U. S. Geological Survey,* pp. 458 to 462 (1908).

Henegan, H. B.: Barite Deposits in the Sweetwater District, Tenn., *The Resources of Tennessee,* State Geological Survey, vol. ii, No. 11, pp. 424 to 429 (Nov., 1912).

Higgins, Edwin: Barytes and Its Preparation for the Market, *Engineering News,* vol. liii, No. 8, pp. 196 to 198 (Feb. 23, 1905).

Hurst, George H.: *Painters' Colors,* pp. 74, 89, 142 (1896). Methods of washing barite, clay, and ocher.

Hutchinson, W. S.: Barytes Deposits at Five Islands, Nova Scotia, *Engineering and Mining Journal,* vol. lxxxiv, No. 18, pp. 825, 826 (Nov. 2, 1907).

Jennison, F. H.: Lake Bases, Their Composition and Uses, *Oil, Paint and Drug Reporter,* vol. lxxxi, No. 11, pp. 27, 28 (1912).

Jones, J. C.: Efflorescence of Brick: *Studies from School of Ceramics, University of Illinois,* vol. iv, No. 4 (Oct. 15, 1906), 22 pp.

Judd, E. K.: The Barytes Industry of the South, *Engineering and Mining Journal,* vol. lxxxiii, No. 16, pp. 751 to 753 (April 20, 1907).

——— A Barytes Grinding Plant, *Engineering and Mining Journal,* vol. lxxxiii, No. 21, pp. 996, 997 (May 25, 1907).

Lakes, Arthur: A New and Large Deposit of Barite in Idaho, *Mining Reporter,* vol. liv, No. 27, p. 162 (Aug. 16, 1906).

Miller, A. M.: The Lead and Zinc Rocks of Central Kentucky, with notes on the mineral veins, *Bulletin No.* 2, *Kentucky Geological Survey,* pp. 24 to 35 (1905).

Mineral Industry, The: vol. ii, pp. 53 to 56; vol. viii, pp. 55, 56; vol. x, pp. 58 to 61; vol. xiii, pp. 32 to 38; vol. xiv, pp. 42 to 45; vol. xv, pp. 65 to 74; vol. xvi, pp. 88 to 96; vol. xvii, pp. 72 to 78; vol. xviii, pp. 60 to 66; vol. xix, pp. 68 to 76; vol. xx, pp. 79 to 91; vol. xxi, pp. 77 to 85; vol. xxii, pp. 42 to 46 (1893 to 1913).

Mineral Resources of the United States, U. S. Geol. Survey: 1901, pp. 915 to 919; 1902, pp. 945 to 948; 1903, pp. 1089 to 1093; 1904, pp. 1095 to 1102; 1905, pp. 1145, 1146; 1906, pp. 1109 to 1114; 1907, Pt. II, pp. 685 to 695; 1908, Pt. II, pp. 669 to 673; 1909, Pt. II, pp. 697 to 700; 1910, Pt. II, pp. 799 to 802; 1911, Pt. II, pp. 965 to 970; 1912, Pt. II, pp. 955 to 959; 1913, Pt. II, pp. 165 to 174.

Norwood, C. J.: Kentucky Barytes and Calcite, *Engineering and Mining Journal,* vol. xciii, No. 9, p. 458 (Mar. 2, 1912).

Poole, H. S.: The Barytes Deposits of Lake Ainslee and North Cheticamp, N. S., with notes on the production, manufacture, and uses of barytes in Canada, *Bulletin No.* 953, *Geological Survey of Canada* (1907). 43 pp.

Singewald, J. T. Jr.: The Barite Deposits at Meggen on the Lenne, *The Tradesman,* April 3, 1913, pp. 32, 33.

Steel, A. A.: The Geology and Preparation of Barite in Washington County, Mo., *Trans.,* xl, 711 to 743 (1909).

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[32] Idem, p. 2355.

——— The Geology and Mining of Barite in Missouri, *Mining World*, vol. xxxii, No. 9, pp. 463 to 467 (Feb. 26, 1910).

Stose, G. W.: Barite in Southern Pennsylvania, *Bulletin No. 225, U. S. Geological Survey*, pp. 515, 516 (1904).

Watson, T. L.: Geology of the Virginia Barite-Deposits, *Trans.*, xxxviii, 710 to 733 (1907); *The Tradesman*, Mar. 20, 1913, pp. 38 to 41; Mar. 27, 1913, pp. 31 to 33.

——— Fluorite and Barite in Tennessee, *Trans.*, xxxvii, 890 (1906).

Watson, T. L., and Grasty, J. S. The Barytes Deposits of Tennessee, *The Tradesman*, May 1, 1913, pp. 34 to 38.

——— The Geology and Barite Deposits of the Cartersville, Ga., District, *The Tradesman*, May 22, 1913, pp. 35 to 37.

Wittich, L. L.: Barytes in Missouri, *Mines and Minerals*, vol. xxxiii, pp. 95 to 97 (1912).

SALINES IN THE OWENS, SEARLES AND PANAMINT BASINS, SOUTHEASTERN CALIFORNIA.*

By **HOYT S. GALE.**†

The salt-incrusted valley floor commonly known as Searles Lake, in southeastern California, has lately come into prominence through the widespread interest in the search for an available source of potash in this country and the apparently promising prospects this locality affords of a considerable production in the near future. The estimate that this deposit contains 4,000,000 tons of water-soluble potash salts, an estimate made with the first public announcement concerning it, in March, 1912, seems to have been amply confirmed by subsequent developments. That this amount of potash salts will actually be produced and placed on the market cannot yet be considered assured, as, of course, the quantity that may be recovered depends on many factors, but so far as can be judged from the evidence available, it seems that this deposit is the most promising immediate source of commercial potash in the United States.

This paper will therefore summarize the history of the waters in which these salts are believed to have been concentrated and through whose ultimate disappearance various saline and other deposits were laid down. Waters that formerly filled Owens Valley until they overflowed, flooding successively lower and lower basins, formed for a time a chain of large lakes in what is now the desert region of southeastern California. These flood waters passed from Owens Valley, the principal source of the water supply, through Indian Wells, Searles and Panamint Valleys, in each of which there was an extensive lake. Finally the waters are believed to have overflowed also into Death Valley, and there the physiographic record has not yet been completely deciphered.

An attempt to understand the lake history of any one of these basins involves a consideration of all the rest, as each played its own independent part in the history of the whole system, and it appears than in no two of the basins is the present result even approximately the same. The extensive saline deposits at the bottom of the Searles Basin are a result of the overflow of waters from the shallow Owens Basin, but they were also influenced by the spreading out of these waters in Indian Wells Valley to form a broad, shallow lake in which the bulk of suspended sediment was probably laid down and beyond which the clarified and concentrating waters drained into the deeper and more isolated Searles Basin. The fact that the Searles Basin for a time overflowed into Panamint Valley and that the Panamint probably overflowed similarly into Death Valley evidently did not prevent the accumulation and deposition in the Searles Basin of an immense mass of solid crystalline salts and mother-liquor brine. It is the purpose to point out in the present paper the more salient distinguishing features and relations of these several basins and to suggest interpretations that may be placed on their influence in saline deposition.

Owen Valley is a long, open, troughlike depression lying immediately west and at the very foot of the highest part of the Sierra Nevada, in Inyo County, southeastern California. It is an extensive basin, about 140 miles in length and 20 to 40 miles in width.

Owens River is one of the few larger perennial streams of the Great Basin region. Its water is derived mainly from the west side of its valley, in tributaries that rise among the snow-covered summits and more or less timbered flanks of the very highest part of the Sierra Nevada. This river constitutes the principal and, in fact, almost the only source of water supply to Owens Lake, other tributaries, such as Cottonwood Creek and springs rising about the shores of the lake, being relatively insignificant.

Owens Lake, the only existing remnant of the former lake system, is a large, shallow body of water in the extreme southern part of Owens Valley. Its water is a dense brine, containing common salt, soda, borax and other salts in solution. The lake lies in a depression which has no outlet, so that its volume depends on its water supply, or on the relation of inflow to evaporation. Owing chiefly to variation in precipitation from year to year, the lake surface is almost constantly changing in height, and the area of its water surface fluctuates considerably with the rise and fall of the water over the broad, flat shores.

As determined by surveys, the area of the water surface in February, 1913, was 62,267 acres, or 97.2 square miles, and the maximum depth of the water was 29.6 feet. The elevation of the water surface at this date was 3,577 feet.

The estimate that over 3,000,000 tons of potassium is dissolved in the Owens Lake water is doubtless not far from correct, but this figure is not intended for direct comparison with the estimates of available potash given for the Searles Lake deposits. The percentage of potash in the Owens Lake water is so much lower than that in the Searles brine that there is much doubt if the Owens Lake water may ever be used for the extraction of this substance, unless it is obtained as a by-product of some other process, or unless the water shall reach a greater natural concentration. There is, of course, a vastly greater amount of potassium in the water-soluble salts in the Searles basin than that included in the 4,000,000-ton estimate.

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*From Bulletin 580-L, U. S. Geological Survey.

†U. S. Geological Survey, Washington, D. C.

The salts now contained in solution in Owens Lake were undoubtedly derived by the slow accumulation and concentration of the river waters entering the basin. As this water supply is and has been continuous, and as there has not been any overflow or outlet except by evaporation for a very long time, it is clear that salts are naturally dissolved in the river waters, though in very dilute solution, have eventually concentrated into the dense brine which is now found in the lake.

Estimates of the total amounts of the various saline constituents contributed to Owens Lake by Owens River are not particularly significant in the present study, for the salts dissolved in the water of the stream, where they exist usually in very dilute solution, undergo many changes on mixing with the standing and more strongly concentrated solution in the lake.

In the foregoing pages the character of the Owens Lake basin and the composition of its river and lake waters have been discussed. During an undetermined though probably a very considerable period Owens Lake overflowed. One period of overflow is probably to be correlated in time with the general expansion of other inland lakes in the Great Basin, such as Lakes Lahontan, Bonneville and Mono, with which, however, it had no direct connection. While the overflow continued the waters in the lake were comparatively fresh, being derived from melting snows and ice fields, chiefly of the Sierra Nevada. Saline material derived from rock decomposition within the tributary drainage area was carried forward with the more abundant water supply in the same way that it is carried in Owens River water today. Since the final cessation of the overflow from this basin, brought about perhaps by a gradually diminishing water supply, concentration by evaporation of the river waters has been going on. The result has been the accumulation in Owens Lake of a great quantity of soluble saline material. The length of time it has taken to accomplish this accumulation is in very general terms about 4,000 years, or possibly considerable less. This period also includes the final desiccation and subsequent alluviation in the other lake basins in the Owens-Searles-Panamint drainage system. Consideration of the further evidence afforded in these other basins follows.

Searles Lake or Marsh, also known as Slate Range Marsh and Borax Flat, is a dry lake basin, superficially much like many other desert basins of the western arid regions of the United States. These names, as generally applied, refer to the broad, flat salt-incrusted surface in the center of the desert basin, although, except as it is intermittently flooded by shallow waters, the region strictly does not contain a lake at all. The basin in which Searles Lake is situated seems to have no generally accepted name, but will here be designated the Searles Basin. It is a broad, roughly circular valley or depression 8 to 10 miles from east to west and 20 to 25 miles from north to south, bordered by the abruptly rising slopes of the surrounding mountain ranges. This basin lies between the Argus Range on the west or northwest and the Slate Range on the east, the latter a narrow rocky wall which divides it from the larger and deeper depression of the Panamint Valley. The camp at the old soda works in the Searles Basin is in the northwest corner of the main desert flat, some 25 miles by road from Searles postoffice, formerly Garden Station, an old stage stop of the overland route through this part of the desert country. Garden Station is now only about a mile east of the branch line of the Southern Pacific Railroad. Searles Lake has been reached by the regular stage that runs from Johannesburg via Garden Station, or Searles, to Searles Lake, and thence on to Ballarat and Skidoo, and passenger traffic doubtless still goes this way, although the branch railroad is now completed, connecting the Searles Basin with the Southern Pacific main line.

The Searles Basin was, during a part of the glacial epoch, occupied by at least one deep lake whose traces are still so distinct as to be indisputable. While the waters stood at their highest position the Searles Basin was flooded to a depth of 635 to 640 feet above the level of the present valley bottom and the lake extended back through the Salt Wells Valley to join with a broad, shallow lake that flooded the greater part of the Indian Wells Valley. With the lowering of the water level less than 75 feet the divide in the volcanic peaks between Indian Wells Valley and Salt Wells Valley became an actual division between two distinct water bodies, and for a time here also there was a period of overflow from Indian Wells Valley to the lower waters in the Searles Basin in the same way that Owens Valley overflowed and spilled its waters into Indian Wells Lake. These are facts attested by the records of the ancient shore lines and water channels.

Horizontal beaches and shore markings over the more rocky portions of the marginal slopes show with great distinctness around the present valley, being preserved in certain localities much more clearly than in others and having been practically removed in still other parts by recent erosion. The old shore lines are more or less marked with deposits of calcareous tufa, in some places amounting to very considerable masses, resembling the tufa deposits of the Lahontan, Mono and Bonneville Basins, described by Russell and Gilbert.

It has been explained that Owens Lake during a period of former greater water supply overflowed the divide at the south end of its baisn and its surplus water flooded in turn a succession of lower basins, of which the Searles Basin was one of the largest. The Owens waters, after passing the Haiwee divide, dropped some 1,500 ft. in about 30 miles to Indian Wells Valley and there spread out in a broad and relatively shallow sheet of water. This in turn also overflowed, its water passing by way of Salt Walls Valley and a rock-cut gorge at the lower end of that valley into the Searles Basin. Eventually the waters rose in the Searles Basin to such a height that all three of these valleys were submerged in one continuous body of water. The maximum water level in this basin was clearly determined by the elevation of an outlet pass on the south side of the basin, whence its surplus waters flowed into the extreme south end of Panamint Valley. In the Panamint Basin a history similar in some respects to that of the Searles Basin was repeated. The waters rose until the height of the lowest outlet was reached, and as they evidently remained stationary at about that level for a relatively long period, it is presumed that this level was determined by the overflow of its surplus water.

The record of these ancient lakes is found in various traces left in the present dry valleys. The discussion of this record, including especially the consideration of the saline deposits left by the evaporating water, is the principal object of this paper.

The area of the former Searles Lake at its greatest expansion, as indicated on the map, was about 385 square miles. This includes both that portion which occupied the Searles Basin and its extension into Salt Wells and Indian Wells Valleys. At this time the level of the waters was evidently determined by the height of the outlet pass on the south side of the Searles Basin, by which the surplus waters found their way into the lower Panamint Valley.

The most distinctive feature of this desert basin is the immense sheet of solid white salts that lies exposed in its bottom. It is to this salt deposit that the name Searles Lake (Searles Dry Lake) has generally been applied. So far as known at present the deposit is unique in this country in the variety of its saline minerals. The immense salt fields in Death Valley are less well known and doubtless contain a larger quantity of sodium chloride and possibly other minerals, but so far as known at present they seem to be of the ordinary playa type, and so of a somewhat different class from the Sealres Lake deposits.

As in other desert basins the valley deposits in the Searles Basin may be distinguished as occupying several more or less distinct areas or zones. These are:

(*a*) The central area of firm crushed salt, constituting what is described hereafter as the main salt deposit. This is variously estimated at 11 to 12 square miles in area.

(*b*) The playa zone, including the central salt area and a broad surrounding margin of salt-incrusted mud and sand, bare of vegetation, composed of salts and mixed alluvial material washed in toward the center of the basin from the surrounding valley slopes. The area of the playa zone is roughly about 60 square miles.

(*c*) The alluvial slopes surrounding the playa zone, composed of detrital material washed from the surrounding mountains and spread out in broad, low, flat alluvial fans, the surfaces generally covered with scattered brush. The materials of which the alluvial slopes are composed are coarser nearer their source at the mountain front and grade off in fineness toward the center of the basin until they merge with the soils in the bare playa zone.

(*d*) The bare rocky slopes of the bordering mountain ranges, which lie beyond and above the alluvial fans and the steeper rock-talus slopes.

The area of salt crust in the Searles Basin is roughly circular as represented on the map, elongated slightly from northwest to southeast, and almost central in the basin. It is believed to be 11 or 12 square miles in extent, as determined by the private surveys and the drilling that has been done. Its surface is the lowest part of the basin and the elevation, determined by spirit leveling in connection with the preparation of the Geological Survey map, is recorded as 1,618 ft. above sea level. In unusually wet seasons surface drainage from the surrounding country sometimes floods the salt surface to a depth of a few inches. Not uncommonly a thin sheet of water, flooded out upon the flat from some local storm, is swept across the surface by the force of the wind, so that perhaps nearly the whole mass of the water is moved from one side of the basin to the other. The surface salt is dissolved to a slight extent by these floods and when it again dries the salt crystallizes with a snowy whiteness that is exceedingly dazzling in the bright sun. Dust storms, which are common to this desert region, scatter more or less dirt over the salt crust and a certain amount of such material is thus almost constantly being mixed with the salt.

The surface of the main or central salt deposit is a firm crust of salt crystals, mostly cubic halite so hard and compact that it will support the weight of a wagon and team or even the heavy drill rig. The surface shows a tendency to crack along irregular lines, so that it is divided into cakes or blocks. Flooding and resolution tend to level inequalities that arise and the cakes and fractures are not so pronounced a feature here as they are on some salt surfaces of similar type elsewhere.

The outline of this central solid salt area is probably not as definite as is indicated by the representation of it on the map, but it is given as interpreted from the borings that were first put down in testing these deposits. The depth of the salts is shown by the drillings to be fairly uniform and it is reported to range from about 60 ft. to more than 100 ft., but probably averaging 70 to 75 ft. in the main part of the deposit. In the central zone the proportion of mud layers found with the salt is comparatively small, so that the mass is in effect a solid body of salts. At and beyond the margin mud is found not only at the surface but intermingled with the salt deposits in depth, so that a sharp delimitation of the main salt deposit would probably be difficult. It is known, however, that the thick mass of solid salts is much more extensive than is indicated by the surface outline of the central salt area, and that a very considerable thickness of crystalline salts underlies a large area which is represented on the surface by playa mud and salt. Just how far this main salt body extends can of course be shown only by drilling.

The salt deposit is in effect a consolidated mass crystallized from an evaporating mother-liquor brine, in which the salts are still immersed, so that it represents a product of desiccating solutions of which the desiccation has not yet been carried to the final stages. Further evaporation of the residual liquor is checked below the reflecting white surface of the salt, and the influx of ground waters and the minor amount of surface waters from the slopes about the basin maintains the balance with evaporation. As a consequence the ground water or heavy saturated brine within the salt mass normally stands at or within a few inches of the actual salt surface. Within the salt mass below the surface the crystalline structure seems to be of such an open cellular or porous nature that the free movement of the ground liquors is not impeded to any considerable degree.

In connection with prospective utilization of the brine by pumping from this deposit attempts have been made to estimate the proportion of brine to solid crystal salts in the mass. The original estimate made in the Government announcement concerning the deposit placed the figure for the brine at 25 per cent by volume of the whole mass. More recent investigation seems to indicate that this figure was much too low. The data on which the later estimates are based are not yet available for quotation, but the interpretation given to them seems to be trustworthy.

The soft mud zone surrounding the main salt deposit contains a very large amount of saline material which doubtless also includes much crystalline salt. Its surface, when dry, is crusted with white salt and is not readily distinguishable from the more solid mass of the central salt area but the proportion of mud mixed with the salts is very evidently greater toward the outer margins of the deposit. The marginal salt and mud zone rises slightly, in general only a few feet, above the level of the central part of the basin and its surface is more irregular. It is saturated with a dense brine which makes much of the surface so soft as to be difficult or impossible to cross. The water is evidently seepage from the higher slopes surrounding the flat. The soft ground extends back until the increasing proportion of coarser material renders its surface sufficiently compact to remain firm.

The chemical composition of the salt and brines in the main deposit has been determined by numerous analyses, special attention having been given in the more recent investigations to the brine that permeates the whole deposit rather than to the salts themselves. For the brine these may be summarized in a fairly simple form by the quotation of a few representative analyses, as the composition shown throughout the deposit, whether in samples from different localities or from top to bottom at one locality, seems to be remarkably uniform. In Table I are given six analyses made by Walton Van Winkle, of the Geological Survey, from as many samples which were collected from different parts of the deposit.

The original brine contains a variable percentage of bicarbonate, which is converted to the carbonate form in the anhydrous residue and is so expressed.

The average analysis has been recalculated to the form of hypothetical anhydrous salts which might be derived from such a brine, as follows.

HYPOTHETICAL AVERAGE COMPOSITION OF ANHYDROUS RESIDUE OF BRINE FROM SEARLES LAKE.

Sodium chloride (NaCl)	51.61
Sodium sulphate (Na_2SO_4)	19.22
Sodium carbonate (Na_2CO_3)	12.79
Sodium biborate ($Na_2B_4O_7$)	3.23
Potassium chloride (KCl)	12.07
Sodium arsenate (Na_3AsO_4)	.17
	99.09

The nature of the deposits underlying the salt mass is known chiefly from one deep well put down on the edge of the flat southeast of the old soda works and some shallower wells that have been sunk only a short distance beneath the salt. The record of the deep well was published in part and has been extensively quoted, as the hole has been the source of a number of entirely new saline minerals.

It appears from this record and the more complete data now at hand that the deposits that fill this basin below the mass of solid crystallized and more soluble salts are chiefly muds, which contain, however, a very considerable amount of chemically deposited material. These deposits may therefore be presumed either to have been laid down during the earlier stages of the former very much deeper Searles water body or to represent in part playa stages of the basin preceding the final lake history. The well record indicates that such deposits extended to a depth of 625 ft. or more below the present valley surface.

Among the more superficial deposits of the region, one feature that deserves mention is the "trona reef." At the eastern and northeastern margins of the main playa zone rises a rim of crusted salts a few feet above the level of the flat and just at the foot of the alluvial slope of sand and coarser wash from the mountains. The deposit is of the nature of a saline efflorescence, being composed of salts brought up with rising ground water and deposited at the surface by evaporation. The "trona reef" at Searles Lake is one of the most massive deposits of this character that has been observed, although this feature is a common one about playa deposits generally, usually showing as a marginal rim of white efflorescent salts about the outermost edge of the bare, flat mud zone.

The trona reef was one of the features that first attracted attention to the Searles Lake deposits—in fact, a single tract of 160 acres at the north end is patented land originally taken up with a view to working these salts. The remains of a large steel-frame machine for hoisting and loading the salt still stand on the ground. The deposit is reported to consist chiefly of trona ($Na_2CO_3.NaHCO_3.2H_2O$), and it is presumed that the material was to have been utilized directly for the production of soda ash. That the trona should have been selectively crystallized in this zone is perhaps somewhat unusual but may be accounted for by supposing it to be a product pertaining to the second or trona stage as illustrated in the experiments on evaporation of the water from Owens Lake.

TABLE I.—COMPOSITION OF BRINE FROM SEARLES LAKE, CAL.

(Percentage of ignited residue. Walton Van Winkle, analyist.)	Well "A 21"	Well "SP 9"	Well "SE 8"	Well "A 14?"	Well "SE 7"	Well "SE 1V"
SiO_2	0.05	0.03	0.00	0.00	0.00	0.03
As	.06	.06	.05	.06	.06	.08
Mg	.00	.00	.00	.00	.00	.00
Ca	.00	.00	.00	.00	.00	.00
Na	33.37	32.57	33.16	33.92	33.23	32.90
K	6.53	7.27	5.98	5.54	6.29	5.69
CO_3	7.37	7.95	6.65	6.89	6.85	6.94
SO_4	12.00	12.49	13.41	11.89	13.79	13.00
Cl	35.97	35.53	36.50	37.13	36.40	36.79
B_4O_7	3.07	1.58	1.77	2.03	2.08	4.14
	98.42	97.48	97.52	97.46	98.70	99.57
Total salts (ignited residue, percentage of original sample)	33.48	33.94	33.30	32.96	33.21	32.88
Specific gravity	1.3002	1.3045	1.2969	1.2935	1.2959	1.2932

The composition of the "trona reef" is expressed in the following analysis, which was made by private chemists but is believed to be representative. It is an analysis of a composite of a number of samples taken from different points on the deposit.

ANALYSIS OF SAMPLES FROM "TRONA REEF," SEARLES LAKE, CAL.

Insoluble in water	13.33
NaCl	19.60
Na_2SO_4	5.05
Na_2CO_3	27.60
$NaHCO_3$	20.60
$Na_2B_4O_7$	1.52
KCl	1.50
	100.00

The composition of pure trona

($Na_2CO_3.NaHCO_3.2H_2O$) is:

Na_2CO_3	46.90
$NaHCO_3$	37.17
H_2O	15.93
	100.00

In the anhydrous salt the proportion

$$Na_2CO_3:NaHCO_3 = 55.79:44.21.$$

Thus the composition given for the trona reef allows for 46.6 per cent of the dehydrated trona, mixed with sodium chloride and other constituents.

Former borax workings about the basin were situated in the margin of the deposits in or near the zone of soft muds and rising ground waters. The mineral ulexite ("cotton ball") is said not to have been found in this deposit, the borax having occurred in the form of natural sodium borate only. The "crude borax" at Searles Lake has been described as found on the surface of the "higher parts of the lake," presumably the slightly more elevated portions of the marginal playa mud zone, in a condition resembling burnt bone. Underlying this material, according to the description, was found a very hard, uneven deposit of different salts, which was generally not disturbed. The "crude borax" was collected to a depth varying from 2 to 8 inches.

There were at least two plants in the former borax workings, the old plant of the San Bernardino Borax Co. situated at the northwest corner of the flat, west of the soda works, an da smaller plant at the extreme north end of the flat, below the station now known as Tanks. The reference by De Groot mentioned above is a description of the equipment and operations of the San Bernardino Co. The surface crust collected from the mud about the margin of the marsh was hauled to the reducing plant, where it was stored in a stack. The stacked material was thrown into dissolving tanks filled with the boiling solution and there kept until it was completely dissolved. Free ammonia is said to have been given off during this process. The heat was supplied through steam coils in the bottom of the tanks, the pipes being pierced with small holes to let off condensed steam. The hot solution, after standing eight hours to settle, was run into long wooden tanks where it cooled and crystallized. In five to nine days crystallization was complete, the product being borax of varying degrees of purity.

According to De Groot, this extensive and valuable deposit of borax was discovered by John W. Searles, who first observed signs of this salt when crossing the marsh that now bears his name, in 1862, at which time he was engaged in prospecting for gold in the Slate Range, lying to the east. Being unacquainted with the nature of the substance, he did not at the time pay much attention to it. Afterward, however, when borax began to be an object of general inquiry he recognized in some samples of this salt shown him the stuff he had noticed while crossing this alkaline flat several years before. Satisfied on this point, he at once took proper steps for locating such portions of the marsh as he considered most valuable.

The deposit is reported to have been located by J. W. Searles and E. M. Skillings on February 14, 1873. Borax was then obtained from the surface scrapings over the mud deposits about the margin of the main salt area, operations which have already been referred to.

Probably the first to suggest that potash might become one of the profitable products of this deposit was Whitman Symmes, who in 1898 was superintendent of the California Borax Co., operating at Searles Lake. Mr. Symmes is said to have at that time located nearly the whole of the salt area of this deposit with the object of working the brine for the extraction of its borax, soda, and potash. The enterprise did not find sufficient support and was allowed to lapse.

In 1908 the whole deposit (41,200 acres, or about 65 square miles) was again located and subsequently was relocated by C. E. Dolbear and seven others for the purpose of establishing there a carbonate of soda or "soda ash" industry. An extensive plant was put in, but for one reason or another the whole equipment was allowed to become idle before any of the soda was shipped.

The announcement of Searles Lake as a possible source of potash, which directed public attention throughout the country to the deposit, was made in a joint press bulletin issued by the United States Geological Survey and the Bureau of Soils soon after the first telegraphic press reports late in March, 1912.

This statement was based on the evidence from analyses of a representative set of brine samples collected jointly from the main deposit early in March by E. E. Free, then of the Bureau of Soils, and the writer. Shortly before the making of this announcement a report had been received that an attempt to exploit the deposit as a source of potash was being made on the basis of three analyses that had been made for this purpose not long before by a firm of private chemists. The materials from which these analyses were made were some sample residues that had been kept from a previous investigation of this deposit with special reference to soda and borax. The three analyses were in effect an afterthought, being made in response to a suggestion concerning a possible potash value in the deposit which came after the original work on the samples had been completed.

Although undue emphasis should not be placed on the fact that the Government agents who examined the deposit thus issued the first public announcement of the deposit as a likely source of commercial potash, nevertheless it is only proper to make clear the circumstances under which these events took place. Only a very few potash analyses from this deposit, made by private persons, showing in any way a potash content in the brines or salts of this deposit were at that time extant. Some apparently extravagant statements had previously been issued, based on what was deemed by many to be insufficient information, the results of a single analysis. In view of this skepticism the Government tests were made and the single potash determination of one of the first of the private tests referred to was substantially confirmed. The announcement quoted above was the first favorable opinion as to any desert-basin saline deposit that had yet been examined in the course of the general field investigation by the Government. This favorable opinion was based mainly on the fact that this basin seemed to fulfill almost entirely the conditions of the hypothesis for the formation of the desert-basin salines on which the field explorations by the Geological Survey had been based.

The prospective development of the Searles Lake deposits is naturally a matter of considerable interest as an enterprise without precedent in this country. According to late advices construction on the new experimental unit in which the American Trona Corporation will begin the manufacture of potassium chloride and other salts from the brine of Searles Lake is progressing. The 31-mile railroad from Searles, on the Southern Pacific Railroad, to the new town of Trona, where the works are being built, is nearly completed. The preliminary plant, it is reported, will handle 20,000 gallons of brine daily, and when the process and equipment have been thoroughly proved by actual operation the works will be enlarged. The salts from the Searles deposit, it is stated, probably will not enter the market regularly until late in 1914. In the meantime a very large number of borings have been sunk through the deposit. This work is intended to serve the purposes of assessment or patent requirements on the claims and to prove the extent and nature of the deposits in depth and area.

Such an undertaking is primarily a chemical manufacturing enterprise, whose success will depend on the utilization of all advantages or economics to be gained by large-scale production and the use or sale of all possible by-products, as well as on the skill developed in handling the physical and chemical problems involved in the separation of the salts. The commodities to be produced are already being supplied in the market, and it is expected that competition for a place in the industry will be keen. The products are bulky and relatively low priced, so that they will suffer the disadvantages of heavy transportation charges in order to reach many of the important markets of the country. Moreover, the initial investment for such an operation is necessarily heavy.

While the waters in the Searles Basin stood at their highest level they undoubtedly overflowed by way of the pass at the south end of that basin and entered the larger and deeper basin of the Panamint Valley. Here they formed the principal water supply of a lake which of course received also contributions of the desert drainage tributary to its valley. This immense body of water, having an origin similar to that of Searles Lake, may have produced the Panamint Valley saline deposits resembling those in the Searles Basin, but there are many qualifying factors to be considered in offering judgment as to whether this is or is not the case.

Panamint Lake was 60 miles in length from north to south and 5 or 6 miles wide for the greater part of its length, though nearly 10 miles wide in the broader portion of the valley north of Ballarat. It was of a different form from the lake in the Searles Basin, being confined in a long, relatively narrow and deep basin, whereas Searles Lake occupied a broad oval basin.

When general interest was first aroused in the subject of potash in the West, attention was naturally directed to all natural accumulations of soluble salts, including "dry-lake" incrustations, residues or efflorescences, mixed mud and salts, and saline or alkaline lakes or well waters. In the testing of these deposits the public very generally participated. It was clearly impossible at that time to define or predict with certainty what classes of materials were most promising as a source of commercial potash, and there was no standard of comparison as to the percentage of potash necessary in a mixture or compound to make it commercially workable. At first the campaign of general, more or less haphazard, testing was entirely justified.

At the same time, however, the dominant idea in the exploration of the desert basins for saline and potash concentrations depended on the assumption of former saline lakes, whose waters by evaporation must have left their salts as massive saline residues. This idea has been referred to as the desert-basin saline hypothesis. At first it was very generally assumed that such lakes had existed in almost all the inclosed drainage basins, chiefly because these areas were alike in not having any present outlet, and the rise of their waters was supposed to have been due to a prevailing more humid climate. On further consideration, however, it is now believed more likely that these ancient lakes were not so widely distributed in the desert-basin region as was at first assumed, and it is even probable that large or persistent water bodies of this type were confined to relatively few areas. Therefore saline concentration in the desert basins may have been going on for long periods under intermittent lake or playa conditions, but the accumulation and deposition of salts in thick crystalline masses as a result of the desiccation of major saline lakes has perhaps been of comparatively rare occurrence. On this basis of reasoning random drilling in the desert basins in the search for large salt deposits is probably not justified from present evidence.

A further conclusion as to saline deposits in ancient lake basins seems warranted. The present ordinary lake waters of the region, such as those of Walker, Pyramid, and Winnemucca lakes, represent accumulations and concentration of tributary drainage waters for a very considerable period. In spite of this fact, if these lakes should dry up their total saline content if deposited as a residue on their dry bottoms would not form a very considerable mass of salts. It is therefore evident that the single filling of such lake basins is not evidence of any considerable saline accumulation in its waters, nor is even the existence of a concentrating reservoir through a long period of time very positive evidence of such a concentration. It therefore becomes important in attempting to estimate the chances of saline deposition from a given lake record to take due account of the probable duration of the concentration period, and this is likely to be a difficult factor to estimate.

The question whether potash would be segregated as a result of saline accumulation in shallow intermittent lakes and the resulting formation of lake deposits has also to be considered. It seems a justifiable conclusion that in such lake beds the potash and other salts would generally be so intimately mixed together or with mud or clay as to be a very unlikely source of commercially valuable materials. Before this idea was generally understood "potash" locations were staked in many of the desert playas and saline flats throughout the desert region. These locations were supported by the "discovery" of small percentages of soluble potash in the surface efflorescences or in the ground solutions of the playa deposits. It is now well known that potash is sparingly distributed in almost all natural saline deposits, and that its presence in small amount has therefore no special significance.

Perhaps the most important factor influencing the disposition of the soluble potash contained in natural drainage waters is the power which clays have of absorbing potash when brought into contact with its solution. It appears that herein lies the actual explanation of the apparent disappearance of much of the potassium salts from solutions or from the saline deposits collected in the desert basins. Although the selective power of clays for absorbing potassium has long been recognized, its influence probably has not been fully appreciated in the discussions of the possible occurrence of potassium salts either in the desert-basin saline deposits or elsewhere in association with other salt deposits. Attention has been repeatedly directed to the low content of potassium as compared with sodium in the desert-basin salines, especially through the many analyses of brines, saline incrustations, and saline muds that have been made during the present investigations. It is significant that certain mud deposits associated with these natural salts have been found to yield unusual amounts of potash, which are not in water-soluble form as obtained in samples, but which readily become soluble on extraction with solutions containing ammonium chloride. The potash appears to be held in the mud either mechanically or in a loosely combined form, and it may have become fixed in this condition by the absorptive action of the muds on the concentrating saline solutions with which they have come into contact.

As a summary, it is probably safe to say that commercially valuable concentrations of potash are not to be looked for in the desert basin deposits generally. In the first place, salines deposited by shallow intermittent lakes are not only so mixed with muds as to render their profitable discovery very doubtful, but such deposits are unlikely to retain on a large scale any considerable percentages of potassium in the soluble form. Only in the basins where large and deep saline lakes have existed and dried up under favorable conditions are massive deposits of salines free from mixture with mud to be looked for. Such conditions are rather exceptional. Probably few desert saline lakes have in fact dried up so free from the mixture of clay or other sediments that their water-soluble salts have retained the major portion of the potash originally present in the lake water.

The confident hope is still held out that these exceptional conditions exist in some places and that by good fortune or otherwise they may be revealed. It seems that in Searles Lake one such exceptional place has been found, and it is possible that there may be even larger and more valuable deposits still to be discovered.

LEAD POISONING IN MANUFACTURE OF STORAGE BATTERIES.

The Bureau of Labor Statistics of the Department of Labor has just published in its Bulletin No. 165 the results of an investigation of storage battery plants in the United States, made by Dr. Alice Hamilton, with special reference to the causes and prevalence of lead poisoning in the industry. The measures for safeguarding workers adopted by Great Britain, Germany, and France are also given.

In the United States there are five large factories making storage batteries, one in Ohio, two in New York, and two in Pennsylvania. A great many smaller plants, employing from 5 to 15 men each, are scattered about the country. This investigation dealt principally with the five large plants.

An ordinary storage battery consists of plates of lead, or of lead grids, covered with a lead oxide paste. In making the plates or grids the worker is exposed to the dusts of the metallic lead and to its fumes when melted. By using hoods and exhausts over kettles and by keeping the work places strictly clean, these dangers can be much reduced. Making and applying the paste involve handling lead oxides, which is much more dangerous than handling metallic lead. The oxides must first be mixed, which is a very dusty job, and then made into paste. Both these operations can be done by machinery under cover, thereby greatly reducing the danger to the worker. In most of the plants visited, however, either such protection was not furnished or it was used so carelessly that it was of comparatively little effect.

In the processes which follow the pasting, such as assembling the plates, lead burning, etc., the worker is exposed to danger from lead fumes and from dust from the dried oxide pastes.

The dangers of the industry can be reduced to a minimum by installing hoods and exhausts to carry off fumes and dusts by substituting machine for hand work, by providing ample washing facilities for the workmen and insisting on strict cleanliness everywhere, and by providing a separate lunch room as the only place where food may be kept and eaten.

The cases of lead poisoning found in storage-battery work are usually acute, with colic and, in severe cases, encephalopathy, but not paralysis. The severer forms of plumbism are not common. Among 64 cases studied 12½ per cent were classed as severe, 39 per cent as moderate, and 48.4 per cent as mild. The period of exposure was not usually long. Of 60 cases studied, 6 had been exposed less than 1 month, 31 less than 3 months, and 50 less than 6 months. Among 12 for whom these facts were secured, one who had been exposed for 2½ months was incapacitated for 3 months, another who had been exposed for 6 weeks was incapacitated for 3 months, and a third who had been exposed for 8 months was incapacitated for only 3 weeks.

In comparison with Germany and Great Britain the storage-battery industry in this country makes a bad showing. In the largest German factory the rate of lead poisoning is less than 1 per 100 employees, and in Great Britain it is about 3 per 100. In the five largest factories here the rate, based on reports known to be incomplete, is almost 18 per 100. The difference is due to the neglect in the United States of factory sanitation and of personal care of the men employed.

EXPORTS OF TIN FROM BOLIVIA.

While the official figures are not available, the approximate exports of tin from Bolivia during 1914, according to the Daily Commerce Reports, were as follows: January, 3,783 metric tons; February, 3,216; March, 3,665; April, 3,477; May, 3,461; June, 3,505; July, 3,426; August, 1,490; September, 1,872; October, November, and December, 6,729. Separate figures for the last three months of the year are not available. The average exports of these three months (2,243 tons per month) as compared with the average for the seven months preceding the outbreak of the European war (3,505 tons) show a falling off of but 36 per cent. The large and rapid rise in price has in large measure compensated for the smaller exports, tin being quoted today (February 14) at £176 ($856), a rise of £26 ($127) during the last seven weeks. This has been due in part to the fact that one cargo of 6,000 tons was sunk.

THE LABORATORY

METHODS OF ANALYSIS USED IN LABORATORIES OF ARMOUR'S INSTITUTE OF TECHNOLOGY.

Written for The Chemical Engineer.

Malt Liquors.

BEER.

Beer is an alcoholic beverage produced from various starch containing substances and flavored with various bitter extractives. The name beer should be strictly applied to the product resulting from the fermentation of barley and hops, unless otherwise qualified. Two distinct processes are employed in the manufacture of beer-malting and brewing.

Malting—Malt is sprouted barley and is prepared by steeping barley in water for several days, draining off the water and "couching" the moist grain (piling in heaps) on a cement floor where it undergoes a spontaneous heating process, during which it germinates, forming the ferment diastase. The amount of diastase is indicated by the length of the sprout or "acrospire" within the grain, and when the maximum yield is reached the germination is checked by spreading the grain in layers over a perforated iron floor and finally subjecting it to artificial heat.

The way in which the green malt is kiln dried largely affects the character of the beer produced from it. When dried between 32° C. and 37° C. a pale malt is then formed, which produces the lightest grade of beer. Most beer is made from malt, dried at higher temperatures from 38° to 50° C., the depth of the color of the liquor varying with the heat to which the malt has been subjected, while the color of the malt varies from the "pale" through the "amber" to "brown" or even black. The darkest grades are sometimes dried at temperatures over 100° C., even to the point where the starch become caramelized.

A more modern method, rapidly coming into use is the so-called pneumatic malting, wherein the whole operation is carried on in a rotating drum, which holds the grain, and in which the temperature and moisture at different stages are carefully controlled by the admission to the interior of the drum of moisture-laden or dry air to the required degree.

The production of diastase is the chief object of malting. This diastase acts on the starch, converting it into the fermentable sugars maltose and dextrin; as malt contains an excess of diastase necessary to convert its own starch to maltose, other starch containing grains such as corn, or rice are mixed with the malt. The excess diastase can convert the starch of a considerable quantity of raw grain. The practice of using other grains than malt is prohibited in some countries.

Brewing—The malt or the mixture of malt and raw grain is crushed and then "mashed" by stirring with water in big vats at a temperature of 50° to 60° C. and then finally heating to 70° C. The conversion of the starch to maltose and dextrin by the diastase of the malt takes place through this process. This liquor is now known as wort and contains besides maltose and dextrin, peptones and amides. The clear wort is drawn off from the residue, and boiled to concentrate and to sterilize. Hops (the female flower of the Humulus lupulus) are then added and boiling continued. The hops contains resins, bitter principles, tannic acid, and a peculiar essential oil, all of which, to some extent, impart flavor to the wort. After cooling and settling, the clear wort is run into fermenting vats. A select variety of yeast, usually saccharomyces cerevisiæ, is added and the alcoholic fermentation allowed to proceed. The fermentation is greatly affected by the temperature. If a slow fermentation is wished for, the temperature must be kept at 5° to 8° C. This is known as bottom fermentation due to the yeast settling at the bottom. If a quick or top fermentation is desired, then the temperature is kept from 15° to 18° C. Here the yeast is carried to the surface by the rapid escape of CO_2 and is removed by skimming. The top fermentation is harder to control than is the bottom fermentation. The race of yeast varies in different localities, according to whether top or bottom fermentation is desired. The beer is drawn off at the proper time, and runs into casks or tuns in which an after fermentation takes place. The beer is then clarified with beech chips or shavings to which impurities and yeast cells attach themselves. The beer after clarification is finally stored in barrels coated with pitch or pasteurized at 60° C. and bottled.

The three principal beers drunk in the United States are of three distinct kinds: Lager beer, Schenk beer and Bock beer.

Lager beer from (lager, a store house) was originally made in the early winter for consumption during the summer. Only a small portion of hops was used in its manufacture. The extract and alcohol were high. This beer was submitted to a prolonged fermentation of four to six months at a low temperature 40° to 60° F. It was called also stock beer.

Schenk beer fermented in four to six weeks was brewed for immediate use in the winter. It was so named, due to the necessity of putting on schenk or draft as soon as made, to keep it from turning sour. This beer is called also, young beer and winter beer.

Bock beer is extra strong and requires about two months in its making. It is intended for spring use and is made in limited quantities, as it is not intended for storage.

Formerly the manufacture of the above three beers depended on the climate, but now with the improved artificial refrigeration the above beers have gradually merged one into the other so that now in the United States the so-called lager beer is made as quickly as the schenk beer.

Berlin Weiss bier is made by fermenting a wort consisting of malted barley, wheat and hops. It is high in carbon dioxide, due to being bottled before the second fermentation is ended. It is prepared by the quick or top fermentation.

Ale is the English name for beer. It is made by the quick or top fermentation from pale malt and is therefore, usually lighter colored than lager beer. It contains a high amount of hops, and a high content of sugar, due to checking fermentation at an earlier stage than in ordinary beer.

TABLE I.

Variety.	Number of Analyses.	Specific Gravities.	Water.	Carbonic Acid.	Alcohol by Weight.	Extract.	Nitrogenous Substances.	Sugar as Maltose.	Gum and Dextrine.	Acid as Lactic.	Glycerin.	Ash.	Phosphoric Acid.
Shenk	205	1.0114	91.11	0.197	3.36	5.34	0.74	0.95	3.11	0.156	0.12	0.204	0.055
Lager	258	1.0162	90.08	0.196	3.93	5.79	0.71	0.88	3.73	0.151	0.165	0.228	0.077
Export beer	109	1.0176	89.01	0.209	4.40	6.38	0.74	1.20	3.47	0.161	0.154	0.247	0.074
Bock	84	1.0213	87.87	0.234	4.69	7.21	0.73	1.81	3.97	0.165	0.176	0.263	0.089
Weiss beer	26	1.0137	91.63	0.297	2.73	5.34	0.58	1.62	2.42	0.392	0.092	0.149	0.034
Porter	40	1.0191	88.49	0.215	4.70	6.59	0.65	2.62	3.08	0.281	....	0.363	0.093
Ale	38	1.0141	89.42	0.201	4.75	5.65	0.61	1.07	1.81	0.278	....	0.31	0.086

Porter is a dark ale. Its dark color should be due to the brown malt dried at high temperature, but is quite often colored with caramel. Its large extract consists chiefly of sugar.

Stout, a name given to extra strong porter, is high in alcohol and extract.

Beer is composed of the following: water, alcohol, sugar, carbon dioxide, succinic acid, dextrin, glycerin, tannic acid, the resinous bitter principles of hops, nitrogenous bodies (chiefly peptones and amides), alkaline and lime salts (chiefly phosphates), fat (traces), acetic and lactic acid. The latter acid constitutes the chief fixed acid of beer.

Table I contains the analysis of different varieties of beer and is due to Konig.

The Board of Health analyzed 15 samples of lager beer and seven samples of pale, bought in Massachusetts bar-rooms. This beer represented as nearly as possible the liquor sold every day to patrons by the bottle or glass. The following is the results:

	Per cent of original wort extract.	Per cent of alcohol by weight.	Per cent of extract.
Beer—			
Maximum	18.91	7.07	7.76
Minimum	7.33	1.10	3.07
Mean	15.04	4.45	5.92
Pale Ale—			
Maximum	15.99	5.37	5.47
Minimum	10.95	3.53	3.38
Mean	13.56	4.49	4.54

Malt and Hop Substitutes: As the price of malt and hops fluctuates in the market, it is often a question of economy to employ cheap substitutes for one or the other. The substitutes for malt may be divided into two classes: First class contains corn, rice and wheat, and is mixed directly with the malt before "mashing" and, like the malt, has to undergo a saccharous fermentation before being acted on by the yeast. The second class contains such substances as cane sugar, invert sugar, commercial glucose, and dextrin. These sugars are added to the wort at a later stage in brewing, just before the addition of the yeast, being in a condition to be readily acted on by the latter.

Glucose is the most common malt substitute, by reason of the fact that its sugars much resemble those of the malt, and are in readily fermentable form. Diastase forms from the malt, dextrin and maltose, while commercial glucose contains dextrin, maltose and dextrose.

When the price of malt is abnormally high, the addition of glucose is decidedly economical, but when ordinary conditions prevail, the cost of the two figured with reference to their yield of alcohol and of extract, is about the same. But the chief advantage of glucose lies in the fact that its use diminishes the nitrogenous content of the wort without lessening the alcohol or extract yielded. Cloudiness or turbidity in the finished product is chiefly due to the nitrogenous matter left after the fermentation of the wort and is sometimes very difficult to remove.

In brewing ales and sparkling pale beers, used for bottling, the use of glucose enhances the appearance very much. A high grade malt may have as much as 40 per cent of glucose added to its wort and still produce an acceptable beer. With low grade malt, glucose yields a very poor quality of beer.

In employing hop substitutes, the question of price enters again. Only when the price of hops is high, is there an inducement to employ substitutes. Quassia wood, chiretta gentian, and calumba, all of which yield bitter principles, have been used in beer, and cannot be considered detrimental to health.

Adulteration of Malt Liquors and Standards of Purity: The Joint Committee on Standards of the A. O. A. C. and the A. S. N. F. D. D. has adopted the following standards:

Malt liquor is a beverage made by the alcoholic fermentation of an infusion, in potable water, of barley malt and hops, with or without unmalted grains or decorticated and degerminated grains.

Beer is a malt liquor and produced by bottom fermentation, and contains in 100 c.c., at 20° C. not less than 5 grams of extractive matter and 0.16 gram of ash, chiefly potassium phosphate, and not less than 2.25 grams of alcohol.

Lager beer or stored beer, is beer which has been stored in casks for a period of at least three months, and contains, in 100 c.c. at 20° C. not less than 5 grams of extractive matters, and 0.16 gram of ash, chiefly potassium phosphate, and not less than 2.50 grams of alcohol.

TABLE II.—COMPOSITION OF 76 SAMPLES OF AMERICAN MALT LIQUORS; ANALYSIS MADE BY PARSONS.

	Specific gravity.	Alcohol by volume.	Extract.	Albuminoids Nx 6.25.	Phosphoric acid.	Ash.	Sulphates in ash.	Free acid.
Average ..	1.0100	5.61	4.61	0.470	0.061	0.209	6.34	0.26
Maximum .	1.0210	7.85	7.64	0.614	0.095	0.296	12.67	0.87
Minimum .	1.0047	0.35	3.15	0.290	0.045	0.147	2.44	0.10

TYPICAL ANALYSIS OF BEERS APPARENTLY NOT BREWED FROM MALT.

Number.	Specific gravity.	Alcohol by volume.	Extract.	Albuminoids Nx 6.25.	Phosphoric acid.	Ash.	Sulphates in ash.	Free acid.
1.....	1.0074	1.68	2.52	0.114	0.010	0.19	21.22	Normal
2.....	1.0098	2.63	3.40	0.215	0.023	0.180	.....	Normal
3.....	1.0062	2.27	2.25	0.150	0.015	0.124	11.30	Normal
4.....	1.0112	2.11	3.53	0.133	0.015	0.140	10.81	Normal
5.....	1.0041	1.85	1.73	0.031	0.010	0.088	12.50	Normal

The ash of the Fifth Sample is thus compared with that of the average beer as given by Blyth:

	Malt Beer. (Blyth).	No Malt Beer. (Parsons).
K_2o	37.22	12.93
Na_2o	8.04	19.61
CaO	1.93	Undetermined
MgO	5.51	Undetermined
Fe_2O_3	Trace	Undetermined
So_3	1.44	10.81
P_2O_5	32.09	10.71
Cl	2.91	21.76
SiO_2	10.82	7.50

Malted beer is beer made of an infusion, in potable water, of barley malt and hops and contains in 100 c.c. at 20° C., not less than 5 grams of extractives matter, nor less than 0.2 gram of ash, chiefly potassium phosphate, not less than 2.25 grams of alcohol, nor less than 0.4 gram of crude protein (nitrogen 6.25).

Ale is a malt liquor produced by top fermentation and contains in 100 c.c., at 20° C., not less than 2.75 grams of alcohol, nor less than 5 grams of extract, and not less than 0.16 gram of ash, chiefly potassium phosphate.

Porter and stout are varieties of malt liquors made in part from highly roasted malt.

Non-injurious bitter principles are without a doubt employed in place of hops and unless the beer is sold for a pure malt beer, they cannot be regarded as adulterants.

Preservatives in Beer: The most common antiseptic found in beer is salicylic acid. Fluorides of ammonium and sodium have been found in American beer. Other preservatives found are benzoic acid and sulphites. The sulphites are mainly due to the "sulphuring" beer casks by fuming calcium bisulphite to thoroughly clean them of any germs that might spoil the beer. Spoiled beer is very often bought by vinegar concerns to use in the vinegar generators for food purposes for the vinegar bacteria.

Temperance Beers and Ales: Many varieties of the so-called temperance drinks are sold on the market. They are usually slightly fermented infusions of various roots and herbs, including ginger and sassafras, with molasses or sugar and yeast. These "soft" drinks generally contain less than one per cent of alcohol by volume. Among them are included spruce beer and the various root beers, such as ginger beer and ginger ale. The latter beverages are generally carbonated. There are numerous brands of bottled beer manufactured, which contain virtually the same body and characteristic flavor as lager beer but not the alcohol. They are made practically the same way and of the same material as lager beer, and then the alcohol is removed by steaming so that the liquor comes within the limit of the temperance beverage. To this class of drinks belongs Uno beer, which ranges from 0.6 to 0.9 per cent in alcohol.

METHODS OF ANALYSIS OF MALT LIQUORS.

Preparation of Sample: The contents of a bottle of malt liquor is transferred to a large flask and shaken vigorously to hasten the escape of carbon dioxide. The temperature of the liquor must be above 15° C. since below this carbon dioxide is retained by the beer and is likely to form bubbles in the pycnometer.

The specific gravity is taken either by a hydrometer spindle in a glass cylinder, by the Westphal balance or by the pycnometer. The latter is far more accurate. The specific gravity is taken at 15.6° or calculated to that temperature.

Ash: 25 c.c. of the liquor is evaporated to dryness then ignited at dull redness.

Alcohol: Be sure sample is rid of carbon dioxide. To do this pass liquor back and forth in large beakers and from time to time remove excess of froth from top of vessel by aid of hand. Continue until liquor is comparatively quiet and free from foam. Introduce 100 c.c. of sample in a flask of 250 to 400 c.c. capacity. Dilute liquor to 150 c.c. and distill into a 100 c.c. flask. The first 75 c.c. of the distillate will contain all the alcohol. The distillate is made up to a 100 c.c., is thoroughly shaken and the specific gravity taken at 15.5° C. by a pycnometer or Westphal balance. From the specific gravity the corresponding percentage of alcohol by weight or volume, or grams per 100 c.c. in the distillate is ascertained by consulting Hehner's table (Food Inspection and Analysis Leach). If liquor is markedly acid, add 0.1 to 0.2 gram of percipitated calcium carbonate previous to distillation.

To obtain percentage of alcohol by weight in the sample, multiply the per cent by weight in the distillate by the weight of the distillate and divided by the weight of the sample taken; to obtain the per cent by volume, multiply the per cent by volume in the distillate by 100, and divide by the volume of the sample used.

TABLE III.—ACKERMANN AND STEINMANN'S TABLE FOR OBTAINING THE PERCENTAGE OF ALCOHOL IN THE DISTILLATE OF BEER FROM THE IMMERSION REFRACTOMETER READINGS.

Refractometer Reading.	Alcohol by Weight, Per cent.	Alcohol by Volume, Per cent.	Refractometer Reading.	Alcohol by Weight, Per cent.	Alcohol by Volume, Per cent.
15.0	0.00	0.00	19.3	2.68	3.37
15.1	0.06	0.08	19.4	2.74	3.46
15.2	0.13	0.16	19.5	2.80	3.53
15.3	0.19	0.24	19.6	2.86	3.61
15.4	0.25	0.32	19.7	2.91	3.68
15.5	0.32	0.40	19.8	2.97	3.75
15.6	0.38	0.48	19.9	3.04	3.83
15.7	0.44	0.56	20.0	3.10	3.90
15.8	0.50	0.64	20.1	3.15	3.97
15.9	0.57	0.72	20.2	3.20	4.04
16.0	0.64	0.80	20.3	3.26	4.11
16.1	0.70	0.88	20.4	3.33	4.19
16.2	0.77	0.96	20.5	3.38	4.26
16.3	0.83	1.04	20.6	3.43	4.33
16.4	0.88	1.12	20.7	3.50	4.41
16.5	0.95	1.19	20.8	3.56	4.48
16.6	1.01	1.27	20.9	3.61	4.55
16.7	1.05	1.33	21.0	3.67	4.63
16.8	1.13	1.43	21.1	3.73	4.71
16.9	1.19	1.51	21.2	3.78	4.77
17.0	1.25	1.58	21.3	3.84	4.84
17.1	1.32	1.66	21.4	3.90	4.92
17.2	1.38	1.74	21.5	3.96	4.99
17.3	1.44	1.82	21.6	4.02	5.06
17.4	1.51	1.90	21.7	4.07	5.13
17.5	1.57	1.98	21.8	4.13	5.20
17.6	1.63	2.05	21.9	4.18	5.26
17.7	1.68	2.12	22.0	4.22	5.32
17.8	1.74	2.20	22.1	4.28	5.39
17.9	1.81	2.28	22.2	4.33	5.46
18.0	1.87	2.36	22.3	4.39	5.53
18.1	1.93	2.44	22.4	4.44	5.59
18.2	2.00	2.52	22.5	4.49	5.65
18.3	2.06	2.60	22.6	4.54	5.72
18.4	2.13	2.68	22.7	4.59	5.78
18.5	2.19	2.76	22.8	4.64	5.85
18.6	2.25	2.84	22.9	4.70	5.92
18.7	2.31	2.92	23.0	4.76	6.00
18.8	2.37	2.99	23.1	4.81	6.07
18.9	2.43	3.07	23.2	4.86	6.13
19.0	2.49	3.14	23.3	4.92	6.20
19.1	2.55	3.22	23.4	4.97	6.27
19.2	2.61	3.29	23.5	5.02	6.33

Alcohol from the Refraction of the Distillate: Prepare the distillate as above except that it is made up to the mark at 17.5° C. The refraction is determined at 17.5° C by means of the immersion refractometer, and the alcohol calculated by the table (Table III) of Ackermann and Steinmann.

TABLE IV.—ACKERMANN'S TABLE FOR OBTAINING THE EXTRACT IN BEER FROM THE IMMERSION REFRACTORY READING OF THE BEER (R) AND OF THE DISTILLATE OF THE BEER (R^1).

$R-R^1$.	Extraction in 100 c.c. Grams.	$R-R^1$.	Extraction in 100 c.c. Grams.	$R-R^1$.	Extraction in 100 c.c. Grams.
15.0	3.76	21.1	5.42	27.2	6.98
15.1	3.88	21.2	5.45	27.3	7.01
15.2	3.91	21.3	5.47	27.4	7.03
15.3	3.93	21.4	5.50	27.5	7.06
15.4	3.96	21.5	5.53	27.6	7.08
15.5	3.98	21.6	5.55	27.7	7.11
15.6	4.01	21.7	5.58	27.8	7.14
15.7	4.04	21.8	5.60	27.9	7.16
15.8	4.06	21.9	5.63	28.0	7.20
15.9	4.09	22.0	5.65	28.1	7.22
16.0	4.11	22.1	5.68	28.2	7.25
16.1	4.14	22.2	5.71	28.3	7.27
16.2	4.16	22.3	5.73	28.4	7.30
16.3	4.19	22.4	5.76	28.5	7.33
16.4	4.22	22.5	5.78	28.6	7.35
16.5	4.24	22.6	5.81	28.7	7.38
16.6	4.27	22.7	5.83	28.8	7.40
16.7	4.29	22.8	5.86	28.9	7.43
16.8	4.32	22.9	5.89	29.0	7.45
16.9	4.34	23.0	5.91	29.1	7.48
17.0	4.37	23.1	5.94	29.2	7.51
17.1	4.40	23.2	5.96	29.3	7.53
17.2	4.12	23.3	5.99	29.4	7.56
17.3	4.45	23.4	6.01	29.5	7.58
17.4	4.47	23.5	6.04	29.6	7.61
17.5	4.50	23.6	6.07	29.7	7.63
17.6	4.52	23.7	6.09	29.8	7.66
17.7	4.55	23.8	6.12	29.9	7.69
17.8	4.57	23.9	6.14	30.0	7.71
17.9	4.60	24.0	6.17	30.1	7.74
18.0	4.63	24.1	6.19	30.2	7.76
18.1	4.65	24.2	6.22	30.3	7.79
18.2	4.68	24.3	6.25	30.4	7.81
18.3	4.70	24.4	6.27	30.5	7.84
18.4	4.73	24.5	6.30	30.6	7.87
18.5	4.75	24.6	6.32	30.7	7.89
18.6	4.78	24.7	6.35	30.8	7.92
18.7	4.81	24.8	6.37	30.9	7.94
18.8	4.83	24.9	6.40	31.0	7.97
18.9	4.86	25.0	6.43	31.1	7.99
19.0	4.88	25.1	6.45	31.2	8.02
19.1	4.91	25.2	6.48	31.3	8.05
19.2	4.93	25.3	6.50	31.4	8.07
19.3	4.96	25.4	6.53	31.5	8.10
19.4	4.98	25.5	6.55	31.6	8.12
19.5	5.01	25.6	6.58	31.7	8.15
19.6	5.04	25.7	6.61	31.8	8.17
19.7	5.06	25.8	6.63	31.9	8.20
19.8	5.09	25.9	6.66	32.0	8.22
19.9	5.11	26.0	6.68	32.1	8.25
20.0	5.14	26.1	6.71	32.2	8.28
20.1	5.17	26.2	6.73	32.3	8.30
20.2	5.19	26.3	6.76	32.4	8.33
20.3	5.22	26.4	6.79	32.5	8.35
20.4	5.24	26.5	6.81	32.6	8.38
20.5	5.27	26.6	6.84	32.7	8.40
20.6	5.29	26.7	6.86	32.8	8.43
20.7	5.32	26.8	6.89	32.9	8.46
20.8	5.35	26.9	6.91		
20.9	5.37	27.0	6.94		
21.0	5.40	27.1	6.97		

Determination of Extract: Where extreme accuracy is desired the result obtained by evaporating at 100° C. a weighed amount of beer is inaccurate due to the dehydration of the maltose at temperature exceeding 75° C. A closer approximation to the truth is obtained, especially with beers high in sugar by calculation as follows:

From specific gravity a measured amount of beer is evaporated to one-fourth its volume on the water bath. Make up to original volume with water and determine specific gravity of the dialcoholized beer. Then by means of Schultz and Ostermann's table (Leach) calculate the extract corresponding.

From the Refraction—Method of Ackermann and Foggenburg: The refraction of the liquor is determined at 17.5° C. by means of the immersion refractometer. The refraction also of the distillate from 100 c.c. is determined at 17.5° C. after making up to its original volume. To secure accurate results care should be taken to cool the prism of the instrument to exactly 17.5° C. by immersing for five minutes in the water bath previous to making the refraction of the liquids. This is not necessary if a number of samples are run except before taking the reading of the first sample.

Calculate the grams of extract (E) from the refraction of the liquor (R) and of the distillate (R) by the following formula:

$$E = 0.25705\,(R - R^1)$$

The extract is more conveniently obtained from Table IV due to Ackermann.

Original Gravity of Beer Wort and Its Determination: A long established custom of the English excise is that the duty on beer is based on the specific gravity of the original wort by which is meant the wort of the beer before any of its sugar has been lost by fermentation.

From the alcohol content in the beer, the sugar originally present in the wort may be calculated, assuming that the alcohol amounts to about half the sugar used up in fermentation.

The specific gravity of the beer is obtained, the beer is then dialcoholized and made up to its original volume, as in the calculation of the extract. This is called the "extract gravity." The specific gravity corresponding to the alcohol found is noted—the specific gravity of the distillate in the alcohol determination when made up to the original volume, and, subtract this from 1. The difference is known arbitrarily as the degree of spirit indication.

From Table V of Graham, Hofman and Redwood, the "degree of gravity lost" corresponding to the "spirit indication" as ascertained. This figure is added to the "extract gravity" to find the "original gravity of the wort."

Example: Suppose the "extract gravity" is 1.0389 and the specific gravity of the alcoholic distillate is 0.9902, both at 15.6° C. Then $1 - 0.9902 = 0.0098$, the "degree of spirit indication." From the above table the corresponding "degree of gravity lost" is found to be 0.0432.

$0.0432 + 1.389 = 1.0821$, the original gravity of the wort.

The calculation above is accurate for normal beer wherein the free acid present, expressed as acetic, does not exceed 0.1 per cent. In case of beer that has developed free acid much in excess of the above limit, a correction should be added to the degree of spirit indication. This correction which in practice is rarely necessary to apply, except in extreme cases of old or sour beer. This is calculated as follows: If (a) represents the grams of free acid (acetic acid) in 100 c.c. then the correction to be added to the spirit indication $= 0.0013a - 0.00014$. Example: Supposing the "extract gravity" to be 1.0413, the specific gravity of the alcoholic distillate to be 0.9890, and the free acid as acetic to be 0.35 per cent. Then $1 - 0.989 = 0.0110$. the "degree of spirit indication."

$0.35 \times 0.0013 - 0.00014 = 0.0003$, correction to be added to the spirit indication.

$0.0110 + 0.0113$, corrected spirit indication.

From the above table the corresponding degrees of gravity lost are $.0506 + 0.0506 + 1.0413 = 1.0919$, the original gravity of the wort.

TABLE V.—SUGAR USED UP IN FERMENTATION.

Degrees of "Spirit Indication."	0.0000	0.0001	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0009
0.000	......	0.0003	0.0006	0.0009	0.0012	0.0015	0.0018	0.0021	0.0024	0.0027
0.001	.0030	.0033	.0037	.0041	.0044	.0048	.0051	.0055	.0059	.0062
0.002	.0066	.0070	.0074	.0078	.0082	.0086	.0090	.0094	.0098	.0102
0.003	.0107	.0111	.0115	.0120	.0124	.0129	.0153	.0138	.0142	.0147
0.004	.0151	.0155	.0160	.0164	.0168	.0173	.0177	.0182	.0186	.0191
0.005	.0195	.0199	.0204	.0209	.0213	.0218	.0222	.0227	.0231	.0236
0.006	.0241	.0245	.0250	.0255	.0260	.0264	.0269	.0274	.0278	.0283
0.007	.0288	.0292	.0297	.0302	.0307	.0312	.0317	.0322	.0327	.0332
0.008	.0337	.0343	.0348	.0354	.0359	.0365	.0370	.0375	.0380	.0386
0.009	.0391	.0397	.0402	.0407	.0412	.0417	.0422	.0427	.0432	.0437
0.010	.0442	.0447	.0451	.0456	.0460	.0465	.0476	.0475	.0480	.0485
0.011	.0490	.0496	.0501	.0506	.0512	.0517	.0522	.0527	.0533	.0538
0.012	.0543	.0549	.0554	.0559	.0564	.0569	.0574	.0579	.0584	.0589
0.013	.0594	.0600	.0605	.0611	.0616	.0622	.0627	.0633	.0638	.0643
0.014	0648	.0654	.0659	.0665	.0471	.0676	.0682	.0687	.0693	.0699
0.015	.0705	.0711	.0717	.0723	.0729	.0735	.0741	.0747	.0753	.0759

Determination of Degree of Fermentation: This is calculated by the formula

$$D = \frac{200A}{B}$$

D. = degree of fermentation.

A. = per cent of alcohol by weight.

B. = the original extract.

Determination of Reducing Sugars: Dialcoholize 25 c.c. of the beer and make up to a 100. Determine reducing sugars by the Defren-O'Sullivan or Munson-Walker method, and calculate as maltose.

Determination of Dextrin: 50 c.c. of the beer are diluted to 200 c.c. hydrolize by heating in a boiling water bath for 2½ hours with 20 c.c. hydrochloric acid (specific gravity 1.125), then nearly neutralize the free acid with sodium hydroxide, make up to 300 c.c., filter and determine the dextrose by copper reduction. Multiply the amount of reducing sugars as maltose by 0.95, subtract this from the dextrose and multiply the difference by 0.9, thus obtaining the dextrin in the beer.

Determination of Total, Fixed and Volatile Acids: A measure volume of the beer, say 10 c.c., is freed from carbon dioxide by bringing to boiling. It is then cooled and titrated with tenth-normal sodium hydroxide using neutral litmus solution an an indicator. Each cubic centimeter of tenth-normal alkali is equivalent to 0.009 gram of lactic acid, in which the total acidity is usually expressed.

Fixed acid, expressed as lactic, though small quantities of succinic, tannic, and malice acids are usually present, is determined as follows: Dealcoholize a measured amount of beer, say 10 c.c., by evaporating to one-fourth its volume, dilute with water to the original volume, and titrate with one-tenth normal alkali, as before.

Volatile acid is expressed as acetic, and is usually calculated by difference between total and fixed acid. Each cubic centimenter of tenth-normal alkali is the equivalent of .006 gram acetic acid.

Determination of Proteins: 50 c.c. of beer are first treated with 5 c.c. of dilute sulphuric acid, and concentrated by boiling to syrupy consistency. Then proceed by the gunning method for determination of nitrogen. $N \times 6.25 =$ proteins.

Determination of Phosphoric Acid: If the sample is not too dark sufficiently close results may be obtained by direct titration of the beer itself with uranium acetate solution.

For the very accurate results proceed as follows: A solution of uranium acetate is prepared of such strength that 20 c.c. will correspond to 0.1 gram P_2O_5. This solution is best standardized against pure, crystallized, uneffloresced, powdered hydrogen sodium phosphate 10.085 grams of which are dissolved in water and made up to one liter. 50 c.c. of this solution contains 0.1 gram phosphoric anhydride if the salt is pure. If the solution is of proper strength, 50 c.c. evaporated to dryness and ignited in a tared platinum dish, should have an ash weighing 0.1874 gram. For preliminary trial about 35 grams of uranium acetate are dissolved in water, 25 c.c. of glacial acetic acid, or its equivalent in weaker acid added, and the solution made up to a liter with water.

To standardize, 50 c.c. of the standard phosphate solution prepared as above are heated to 90° or 100° C., and the uranium solution run in from a burette till the resulting precipitate of hydrogen uranium phosphate is complete. The end point is determined by transferring a few drops of the solution to a porcelain plate, and touching with a drop of freshly prepared potassium ferrocyanide solution. When the slightest excess of uranium acetate has been added, a reddish-brown color is produced by the ferrocyanide. The uranium acetate solution is purposely made rather stronger than necessary at first, and by repeated trials is brought by dilution with water to the required strength (20 c.c. equivalent to 50 cc. of the phosphate solution).

Fifty c.c. of the beer are heated to 90° or 100° C. and titrated with the uranium acetate solution under the same conditions and in precisely the same manner as when standardizing that solution. Each cubic centimeter of the uranium acetate corresponds to .01 per cent of P_2O_5.

For the phosphoric acid determination in the ash, 50 c.c. of the beer are incinerated in the usual manner, and the ash moistened with concentrated hydrochloric acid. The acid is then evaporated off on the water bath, after which the ash is boiled with 50 c.c. of distilled water and titrated with the standard uranium solution.

Detection of Bitter Principles: The bitter principles of hops is readily soluble in ether, when a sample of beer is evaporated to syrupy consistency is extracted therewith, while the bitters of quassia and aloes, common hop substitutes, are insoluble in ether. Though many varieties of bitters might be employed that are soluble in either, the absence of a bitter taste from the ether extract is evident of the absence of hops.

The most marked difference between hops and their substitutes in malt liquors lies in the fact that the bitter principles of hops is completely precipitated therefrom by treatment of the beer with lead acetate (either basic or neutral), leaving no bitter taste in the filtrate after concentration, while if any of the hop substitutes are present, the concentrated filtrate from the lead acetate treatment will have a bitter taste. The excess lead should be removed from he filtrate, before concentrating and tasting, by treatment with hydrogen sulphide. If the residue from the ether or chloroform extraction of the concentrated filtrate from a beer after treatment with lead acetate be found to be bitter, here is positive evidence that a foreign substitute has been employed.

In the following some characteristic reactions are given that may help to identify some of the common hop substitutes.

Quassim is readily soluble by chloroform from acid solution. If a residue containing quassiim be moistened with a weak alcoholic solution of ferric chloride and gently heated, a marked mahogany-brown coloration is produced. On treatment of quassiim with bromine and sodium hydroxide or ammonia, a bright-yellow color is shown.

Chiretta is readily dissolved by ether from its aqueous solution. Its ether residue, when treated with bromine and ammonia, gives a straw color, slowly changing to a dull purple-brown. This is not true of its chloroform residue, so that it is not to be mistaken for quassia.

Gentian bitter may be extracted by treatment of the acid liquor with chloroform. When the residue containing gentian bitter is treated with concentrated sulphuric acid in the cold, no color is produced, but on warming gently a carmine-red color is shown; if further treated with ferric chloride solution, a green-brown color is formed.

Aloes—200 c.c. of the beer are evaporated, dried and treated with warm ammonia, filtered, cooled, and treated with hydrochloric acid. The resin of aloes is precipitated and collected on a filter. It is insoluble in cold water, ether, chloroform, or petroleum ether, but is soluble in alcohol. It has a very characteristic odor which serves to identify it. The hot-water solution gives a curdy precipitate on treatment with lead acetate.

Capsicin is extracted by treatment of the acid liquor with chloroform. It is recognized by its sharp, pungent taste.

MALT EXTRACT.

True malt extract is a syrupy fluid having specific gravity of from 1.3 to 1.6 and made up in accordance with the following directions of the 1880 Parmacopoeia. Upon 100 parts of coarsely powdered malt contained in a suitable vessel, pour 100 parts of water, and macerate for six hours. Then add 400 parts of water, heated to about 30° C. and digest for an hour at a temperature not exceeding 55° C. Strain the mixture with a strong pressure. Finally, by means of a water bath or vacuum apparatus, at a temperature not exceeding 55° C., evaporate the strained liquid rapidly to the consistency of thick honey.

Keep the product in well closed vessels in a cool place.

A residue like this has an extract of at least 70 per cent, consistency chiefly of maltose, and contains about 2 per cent of diastase. It should furthermore be capable of converting its own weight of starch at 55° C. in less than ten minutes.

Table VI gives analysis of the pure malt extract.

TABLE VI.

	Specific Gravity.	Alcohol.	Extract.	Free Acids, as Acetic.	Volatile Acids.	Albuminoids.	Maltose.	Dextrine.	Ash.	Phosphoric Acid.	Diastatic Action.
A......	1.387	0	72.31	0.231	0.033	3.329	62.52	5.25	1.21	0.483	Complete in less than 5 minutes
B......	1.421	0	76.65	0.275	0.021	3.116	65.41	6.94	1.19	0.556	Complete in less than 10 minutes
C......	1.498	0	79.81	0.386	0.053	4.872	61.32	12.39	1.23	0.428	Complete in less than 5 minutes

There are on the market many so-called malt extracts widely advertised for their tonic and medicinal virtues, having the taste and consistency of beer or ale. They are virtually beer in fact, differing therefrom mainly in respect to price. Such malt extracts have no diastase, and their value as nutrients depends almost entirely on their sugar content.

Harrington has analyzed 21 of the best known of these alleged malt extracts, the maximum, minimum and mean results of his analysis being as follows:

	Specific Gravity.	Alcohol.	Total Residue.	Ash.
Maximum	1.0555	7.13	13.63	0.23
Minimum	1.0149	0.74	5.13	0.20
Mean	......	3.94	8.78	....

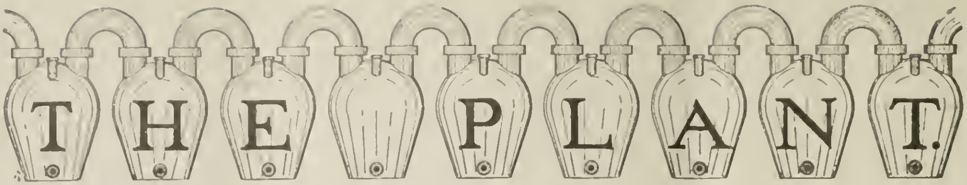
TIN OUTPUT OF FEDERATED MALAY STATES.

The restricting effect of the European war on the tin industry of the Federated Malay States is seen in the decline of 2,429,333 lbs., by which amount the output for 1914 fell short of that for 1913, according to the Daily Comerce Reports. The decrease in value was $2,048,620 United States gold.

The whole year was a discouraging one. Some time prior to the outbreak of hostilities the industry suffered from low prices, and, of course, with war in progress there was slight chance of a recovery in values. The natural result was a falling off in production. The total output for 1914 is officially given as 109,854,533 lbs., against 111,283,867 lbs. in the preceding year. The small mines were forced to close down, and even the larger ones had to restrict operations. It is declared that 25 per cent of the coolies in the country have been repatriated; that fact in itself is a clear indication of the extent to which operations were reduced.

The tin industry is an important factor in the local commercial life, and the offer of the local government at the outbreak of war—when all commercial activity was seriously interfered with—to buy up the total tin output at a specified price ($34.05 United States gold per picul of 133⅓ lbs.) can well be said to have averted a crisis in this community. The tin market is now showing signs of improvement, prices reaching $43.70 per picul a day or two ago.

Shipments of tin to America during 1914 amounted to 22,032,267 lbs., as compared with 26,222,133 lbs. in 1913.



PICRIC ACID: ITS MANUFACTURE AND LIABILITY TO EXPLODE.

By THOMAS OSBORNE.

Written for The Chemical Engineer

Factories in which picric acid is made are subject to explosions the nature of which is somewhat obscure, Several have occurred within recent years involving serious loss of life. In the consideration of the most probable cause of accidents, two separate and distinct questions are suggested for consideration; first, the means by which the heat necessary for ignition can be produced, and secondly, explanation of the conditions or circumstances by which, contrary to all preconceived ideas, the ignition should at once develop into explosion, instead of merely resulting in comparatively harmless combustion. Works for the manufacture of picric acid may consist of two groups of buildings, one in which the wet process of manufacture is carried on and another in which the acid is dried, sifted, packed and stored.

Process of Manufacture.—The process of making picric acid consists broadly in mixing carbolic acid with strong sulphuric acid, diluting this sulphonate with water and then running it slowly into nitric acid. The mixture is allowed to cool when the crude picric acid crystallizes out and is subsequently purified by re-crystallization. After thorough washing with water to remove all traces of free nitric and sulphuric acids, the material is whirled in a centrifugal or hydro-extractor to remove the bulk of the water and is then removed to the drying shed, where it is spread on glass beds heated by steam until all moisture is removed. It is then transferred in large open drums to the sifting-room where it is ground and passed through a revolving sieve, whence it is taken to the packing room and packed in barrels. The large crystals which fail to pass through the sieve are ground in a crushing mill and then added to the rest.

Experience and records suggest that it should be impossible that an explosion of unconfined picric acid should occur, provided that the quantity in any one building is limited to a moderate amount and that no picrates are present. Under ordinary conditions the risk is one rather of fire than of explosion, consequently the buildings are not usually placed very far apart; as they undoubtedly would be if explosion were an ordinary risk. In the case of one explosion the whole quantity of loose picric acid appears to have detonated without warning and to have communicated sympathetically to other buildings in which unprotected acid was present. The hitherto accepted theory that picric acid cannot be exploded by friction or heat, unless confined is open to doubt. One process of the manufacture may be said to be never entirely free from risk; that is, the operation of grinding the larger crystals of picric acid which have failed to pass through the sieve. To effect this the picric acid from the drying shed is usually by means of a hopper introduced into a revolving sieve or reel, turned by hand; all the material passing through the meshes of the sieve falls on the floor and is removed by raising a hinged shutter at the floor level in the casing enclosing the reel. Such of the crystals as are too large to pass through the sieve are removed and transferred to the grinding mill. This mill is constructed of iron and generally consists essentially of a pair of revolving discs to which the material to be crushed is fed through a hopper. The machine is so made as to be easily taken to pieces for cleaning purposes and put together again, a process generally done daily at the end of the day's work; it can be cleaned by means of a handbrush and cloth. The operation of sieving is simple enough and presents no dangerous features; moreover picric acid is by no means easy to ignite, especially when the reel is turned by hand; so that there appears to be little probability that accidents can occur at this stage, there seems to be a much greater probability that ignition may occur in the grinding mill. In one factory no less than three fires have occurred within the last few years during the operation of grinding the dry acid. The mere process of grinding is not necessarily dangerous, that may be inferred from the fact of the immunity experienced during the operation of drilling out the primer space in the solidified charges of picric acid filled into shells and ammunition, by means of power-driven steel drills, a method which has been employed in Europe for some time without the slightest accident. But because picric acid may be safely ground in an iron mill, that does not apply to nails, stones and other hard foreign bodies, which may accidentally find their way into the powdered material. In one case of a fire an examination showed that it was produced by the pressure of a nail in the machine. Apart from ignition there is explosion to be considered, which occasionally immediately follows and it seems quite possible from recent experience, that it may be desirable to modify to a very considerable extent the conditions under which the manufacture of picric acid is now carried on, so as to ensure the safety of those engaged in the factories. In the case of one disastrous explosion it was established beyond the possibility of doubt, that it was due not to picric acid alone, but to the presence of considerable quantities of lead and strontium compounds, which under the influence of heat and in contact with the melted picric acid led to the formation of lead and strontium picrates, both of which and more particularly the lead salt, are not only in themselves violently explosive, but are capable of detonating picric acid in contact with them. It is noteworthy that it is stated in books on the subject by chemists of the highest standing, that when suddenly heated, picric acid will explode; it is not possible to obtain confirmation of the statement in the actual experience of manufacturers, or from the accounts of accidents which have taken place, or from experiments instituted for the special purpose of clearing up the point. In fact so far as experience, records and experiments go, they may all be said to furnish a very emphatic contradiction of the statements, that picric acid when unconfined can be exploded by fire. A case is recorded in which an iron vessel with a very small orifice and containing 25 lbs. of picric acid was placed in a reverberatory furnace, when the acid burned away without explosion.

On the other hand, it has been found quite possible to explode picric acid by a blow, but this blow must be of considerable force if the material is cold and of a character that could seldom occur in practice—all experience, in fact, seems to prove as surely as negative evidence can be said to prove anything, that it may be taken as a practical impossibility for picric acid to explode without giving sufficient warning by fire to enable anyone in the vicinity to escape, and that, moreover, a fire in its initial stages can be extinguished by water without much difficulty.

In Great Britain, as the result of explosions due to causes, which have never been ascertained, picric acid is regarded as an explosive and a license has to be obtained for its manufacture, but conditions of a drastic nature are not imposed and no limit was placed on the quantity that may be present in a building. Some years ago a serious explosion occurred in the north of England at picric acid works. It was suggested by experts after careful inquiry, that it occurred after a fire had been raging for nearly ten minutes and that it was probably due to the formation of picrates of lime from the mortar in the roof of one of the buildings that fell in; moreover, that it could not be stated with certainty that it was not caused by the picric acid alone, which was present in greater quantity than in any instance quoted to establish the contrary view. More recently the quantity has been limited, that may be present in any one compartment; 2,000 lbs. is now considered the maximum which may be allowed in one risk. It is also considered desirable to have sprinklers fitted to every comparment or building liable to contain dry picric acid, as the danger of a fire developing into explosion is considered so slight as to be negligible.

In an accident which occurred last December the explosion was not preceded by a fire, the flash and report were simultaneous and experts are extremely reluctant to accept the possibility that the explosion was due to picric acid pure and simple; had a fire been in progress for even one minute there might have been some justification for attributing the cause merely to the presence of a substantial quantity of the acid. There seems to have been no possibility that by any means or other a picrate could have become mixed with the acid, owing to the simplicity of the process of manufacture and the careful method of construction of the buildings. A possible cause of explosion is the presence of dust in the atmosphere; it may accumulate for a considerable period of time, then a combination of circumstances may disseminate it throughout the room; a strong wind from an unusual direction, a draught through an open door would churn it up, and there are the raw materials for an explosion. Explosions have occurred in flour mills, the danger of coal dust explosions in dry and dusty mines is well known and even oil cake dust has not so very long ago led to a serious disaster. The fact that each molecule of picric acid dust contains all the elements of an explosive would of course tend to increase the violence of the explosion. Thus given the presence of a nail or stone in the grinding mill and a cloud of dust raised by some accident, then all the elements to produce an explosion are provided.

IMPORTS OF POTASH SALTS IN FEBRUARY.

Public interest in the statistics regarding imported potash salts is keen, both by reason of their wide application in the manufacturing and other industries and the fact that the United States is still dependent upon foreign countries for practically the entire supply thereof. The following table, from the Daily Commerce Reports, shows the imports of potash salts during the month of February, 1915, compared with February of last year. The figures are so grouped as to show those potash salts used chiefly as fertilizers, which are entered by the long ton, and those which are used in the arts and chemical industries, of which the unit of quantity is the pound.

Articles exported	February, 1914.		February, 1915	
Fertilizer salts:	Quantities.	Values.	Quantities.	Values.
Kainit ....tons	72,008	$321,723	1,852	$ 18,445
Manure salts ..... do.	12,451	124,422	900	14,748
Sulphate of potash. do.	5,098	210,327	1,378	59,804
Muriate of potash.. do.	13,172	431,820	22,818	836,368
Other potash salts:				
Carbonate of potash lbs.	1,674,685	49,110	1,317,849	46,015
Caustic potash..... do.	520,166	19,607	308,805	17,508
Nitrate of potash.. do.	22,699	928	....	......
Cyanide of potash. do.	5,641	890	266,654	39,327
Other potash salts. do.	638,112	52,119	456,011	42,429

The British Foreign Office states that the demands upon the limited output in Great Britain of aniline oil and aniline salts (recently placed on the British embargo list) make it necessary to consider only applications for shipment in reduced quantities.

THE "CRACKING" OF HYDROCARBONS.

By B. B. FREUD.

Written for The Chemical Engineer.

That carbon compounds decompose at relatively low temperatures has always been recognized as a characteristic difference between those compounds and the compounds of the other elements. That such decomposition is looked upon as an instance of the phenomenon of dissociation is not always the case. Hence it is that we have coined the special word "cracking" when discussing the formation of low boiling hydrocarbons by the action of heat energy upon higher boiling ones, while the closely analogous formation of ammonia and hydrogen chloride by heating ammonium chloride is a reaction characterized by the apparently perfectly understood word—dissociation. That the mechanism of the various types of dissociation reactions is imperfectly understood, is only too well known to the physical chemist. But in spite of this, when petroleum "cracking" is identified with thermal dissociation and when the ideas of the latter are applied to the former, the chemical changes that take place in this reaction will become less mysterious. From the accidental discovery in 1861, at Newark, of the "cracking" effect of high temperatures on petroleum, to the recent observations of Bacon, Rittman, Snelling, Brooks, Burton and others, all of the facts are qualitatively, at least, what we should expect from our accepted ideas of dissociation.

Hydrocarbons of smaller molecular weight are more stable than those of larger molecular weight. So it was perfectly natural to expect that since larger amounts of "kerosene" were actually obtained from a given crude oil that had been heated to a high temperature than were obtained from the same crude oil that has merely been fractionated, similarly larger amounts of "gasoline" would be obtained if the crude were subjected to a still higher temperature before fractionation. The results justified the expectation. The nature of this dissociation is not known. Nef has been explaining it for years on the basis of methylene dissociation. If we suppose our original petroleum to be composed of molecules of the formula $CH_3 — (CH_2)_m — CH_2 — CH_2 — (CH_2)_n — CH_3$, we can imagine that dissociation might take place to form $(CH_3) — (CH_2)_m — CH_3$, $H\rightarrow$, and $\leftarrow H_2C\ (CH_2)_n — CH_3$. The $H\rightarrow$ might unite with the $\leftarrow H_2C\ (CH_2)_n — CH_3$ to form $CH_3\ (CH_2)_n\ CH_3$, and the alkylidene $(CH_3)\ (CH_2)_n — CH$ not being capable of existence, would rearrange nonreversibly to form the olefine $CH_3\ (CH_2)_m —{}_1CH = CH_2$. Thus we have formed from a paraffin molecule, two smaller ones, one a paraffin and the other an olefine. The amount of this dissociation depends upon the temperature to which the original molecule was heated. Thus we find the amount of olefine in cracked petroleum (at one atmosphere) ranging from 20 to 50 per cent, the more olefine the higher the temperature of cracking.

But the reaction need not be as simple as indicated. For instance two of the alkyl groups $\leftarrow CH_2\ (CH_3)_n\ CH_3$ might unite to form the paraffin $CH_3\ (CH_2)_{2n} +{}_2 CH_3$, of a possibly greater molecular weight than the original molecule; two of the dissociated hydrogen atoms $H\rightarrow$ simultaneously would unit with one alkylidene $CH_3\ (CH_2)_m\ CH\rightarrow$ to form the paraffin $H_3\ (CH_2)_m\ CH_3$; the other alkylidene $CH_3\ (CH_2)_m\ CH\rightarrow$ would rearrange nonreversibly to the olefine $CH_3\ (CH_2)\ ({}_m —{}_1)\ CH = CH_2$. Or one of the dissociated hydrogen atoms could add to one each of the alkylidene groups to form two alky groups $CH_3 — (CH_2)_m\ CH_2\rightarrow$, which would unite to form the paraffin $CH_3\ (CH_2)_{2m} +{}_2 CH_3$. Thus we see that on the mere assumption of the dissociation of the paraffin molecule $CH_3\ (CH_2)_m\ CH_2\ CH_2\ (CH_2)_n\ CH_3$ at a definite place in the molecule we can get the paraffin molecules, $CH_3\ (CH_2)_n\ CH_3$, $CH_3\ (CH_2)_{2n} +{}_2CH_3$, $CH_3\ (CH_2)_m\ CH_3$, $CH_3\ (CH_2)_{2m} +{}_2CH_3$, and the olefine molecule $CH_3\ (CH_2)_m —{}_1CH = CH_2$. When it is considered that dissociation may take place at many different places in the molecule, that is the m and n in the illustration may be anything so long as, for that molecule, the m's plus the corresponding n's are constant, the number of possible alignments is very large. Smaller and larger molecules, paraffins and olefines can thus be formed in the "cracking" operation, the relative amounts of the various products depending on the nature and degree of the dissociation.

Nor are the possibilities exhausted yet. It is known that olefines are in general less stable than paraffins of the same number of carbon atoms; that polymethylenes are more stable; that unsaturated hydrocarbons condense to more saturated ones especially at higher pressures; that olefines polymerize. Hence it is to be expected that the new alignments first formed as a result of the dissociations will readjust themselves to the more stable forms under the new conditions. Thus the transformations that may take place in the "cracking" reaction are bewilderingly complex; and are followed analytically with the greatest difficulty, if at all. The evidence for this interpretation is a matter of record in the enormous literature of the subject. It is nicely summarized and extended by Brooks, Bacon, Padjett and Humphrey in the Journal of Industrial and Engineering Chemistry, Vol. 7, No. 3, on the "Preparation of Gasoline and Kerosene from Heavier Hydrocarbons," from which many of the facts of this article are taken.

Having recognized that the general principle of dissociation, in its broad sense, applies to the "cracking" reaction, and having seen the possibility of producing large numbers and many varieties of products it is natural to make as the next step, the investigation of the influence of varying conditions on the nature of the reaction. The influence of variations in temperature and pressure, the effect of the concentration of the original molecules and the final ones, the concentration of the liquid and gas phases have all been noted. Thus the subject becomes merely an application of the fundamental generalization of heterogeneous equilibria, the phase law, and likewise of the fundamental generalization of homogeneous equilibria, the mass action law. And since we are not necessarily keeping these variables at definite values indefinitely or until equilibrium has been achieved in the reaction, the question of time is very important. Also must be considered those factors which influence the effect of time, namely, the presence of catalysts, and the area of contact between the hot surface and the oil and between the liquid and gas phases. The developments of the "cracking" reaction culminating in the method of Rittman of having the reaction take place in the absence of the liquid phase has been due to the application of the physico-chemical principles mentioned. All too often this application has been made unconciously; but particularly in the more recent work, the successes have been due to investigations based on the intentional applications of these definite considerations.

The first observation, of course, was the effect of temperature on the liquid phase at ordinary pressures. Then it was found that if the "cracking" was done at higher pressures the amount of olefine was less. Likewise at higher pressure, in spite of the higher temperature necessary to maintain it, the amount of hydrogen in the evolved gases was less. Hence the simultaneous use of higher pressures with high temperatures to get a product richer in saturated hydrocarbons than is obtained by the use of high temperature alone. Whether the smaller amounts of olefine is a result of hydrogenation under the new conditions as is plausible from the work of Whitaker and Rittman, or whether the saturated hydrocarbons are formed simultaneously with the appearance of the dissociated hydrogen and olefine (or alkylidene) as is indicated by Bacon, cannot be determined at present.

The first processes using increased pressure, merely applied the pressure during the "cracking" operation, and subsequent distillation was effected after pressure was released. This was followed by actual distillation as well as "cracking," under pressure. Young used a pressure of 10-20 pounds, Krey of 2-4 atmospheres, Boleg of 3-6 atmospheres, and Bacon and Clark of 100-300 lbs. The success of the Burton process, at present in successful operation, is supposed to be due to this distillation under pressure. Burton claims that if the pressure valve is between the still and the condenser thus conducting the actual distillation at ordinary pressure large amounts of olefine are formed, while if the pressure valve is placed after the condenser thus conducting the distillation as well as the heating at the same pressure (75 pounds) no olefines are formed. Bacon and his collaborators question the fact that this result is due merely to the position of the valve. And their point is well taken because we know that olefines do not polymerize under these conditions. Burton's claim is a question of fact that can easily be determined by experiment. Aside from the conflicting evidence on this point, we can be sure that the efficiency of the Burton process is due to the relatively larger volumes of the vapor phase in the reaction. This conclusion is justified by Snelling's observations, mentioned later.

The next stage in the development of the "cracking" operation is the total elimination of the original liquid phase. This is one of the important conditions in the new Rittman process. In a private communication to the author Rittman says "the higher the pressure one uses in cracking over oil to gasoline the more saturated are the gasoline hydrocarbons produced. I have not been working at pressures exceeding 600 pounds, but up to that pressure there is a continuous advantage gained by increased pressure." In Scientific American of March 20, 1915, is a description by C. H. Claudy of the Rittman method. The oil is vaporized and admitted into the reaction chamber in the form of vapor in sufficient quantity to maintain the pressure desired. In the earlier liquid vapor methods, pressures of 100 pounds are high. In the Rittman vapor method pressure of 500 pounds is easily obtained, safe, and under perfect control, as is also the temperature which is more or less uniform throughout the reaction chamber. Another important condition in the Rittman process is the removal of the products of the reaction from the reaction chamber. This of course, is merely an application of the law of mass action; the removal of one of the products of the reaction so as to permit it to go to completion. Thus in this process the heating and pressure are applied to the vapor phase alone, both the original and final liquid phases being eliminated from the reaction chamber. Of course, the final liquid phase is subject to fractionation as usual. It will undoubtedly be found that fractionation under pressure will give the better results for although gasoline hydrocarbons are rather stable they are slowly decomposed in the "cracking" operation, and should be removed from the heavier hydrocarbons in the reduced oil under similar conditions to those under which they were formed, and also removed as soon as formed. While it should be stated that the Rittman process is only in the laboratory state, there is little doubt in the author's mind but that it will be commercially successful. This fact will soon be known definitely as arrangements have been made whereby the Aetna Explosive Company has agreed to test and develop the process under the direction of the Bureau of Mines, at a plant in Pittsburgh. The company has undertaken to devote $200,000 to the investigation.

The very striking and unique claim for the Rittman process is that under similar conditions and without material change in the apparatus it is possible to obtain rather large amounts of aromatic hydrocarbons of the type of benzol and toluol with varying quantities of mesitylene, naphthalene, and anthracene. Dr. Rittman has written the author to the effect that his "work of the last two years seems to indicate that the end products of petroleum cracking are primarily a function of temperature, pressure, concentration and time prevailing; in other words, one reaches the same goal regardless of the type of oil used. In other words, say at a temperature of 650° C. and 15 atmospheres pressure, one obtains good yields of aromatic hydrocarbons regardless of whether he starts with an Oklahoma, a California, a Russian, or a Pennsylvania oil."

Since in the Burton process none or but very small amounts of aromatic hydrocarbons are produced, while in the Rittman process oil containing no aromatic hydrocarbons and passed once through the process is shown to contain as much as 6 per cent of benzol and toluol, it seems that the conditions necessary for the formation of aromatic hydrocarbons are merely higher temperature and pressure than are necessary for the formation of the gasoline hydrocarbons. This is verified by a report of the Rittman method given in the Oil, Paint and Drug Reporter for March, 1915, which states that "the temperature is given for thus producing gasoline at 450° C. and above, and the pressure of about 90 pounds per square inch; whereas, with the same apparatus or process in producing larger percentages of benzol and toluol the pressure and temperatures used are increased up to the following figures: temperature 500° C. and pressures above 100 pounds per square inch." Thus it becomes clear why the older "liquid-vapor" processes with their limited temperature and pressure ranges do not yield aromatic bodies, while the newer "vapor" process with its possibility of higher temperatures and pressures, does not result in their production. The fact of the formation of aromatic bodies is not peculiar, when we consider that there is no really fundamental difference between aromatic and paraffin hydrocarbons. Organic chemists have been emphasizing this for many years by showing that it is possible to pass from one to the other and back again by chemical transformations, and by showing that the reactions of one class are, with a difference in degrees, the reactions of the other. Also it is known that if methane is heated in the absence of air ethylene is formed, among other things. This on similar treatment, gives some acetylene. Likewise benzene, naphthalene, and finally carbon are formed on continuing the treatment. So there is nothing peculiar in the formation of aromatic hydrocarbons by the "cracking" process. However, as to the method of their formation, it should be said that Brooks, Bacon, etc., believe that aromatic hydrocarbons are not produced directly or indirectly by a process of dehydrogenation. They believe that benzene, toluene and xylene split off from large so-called petroleum hydrocarbons which already contain the phenyl radical. In this connection they refer to Jones and Wheeler who have shown that aromatic hydrocarbons are produced in the distillation of coal at 350°, or below the temperature at which hydrogen is split off. Brooks, Bacon, etc., have also obtained aromatic hydrocarbons by the action of $AlCl_3$ on reduced Oklahoma oil, by a sort of reversed Friedel and Crafts reaction.

Like all chemical reactions this one can be influenced catalytically. Patents are described using steam, steam and iron, steam and other metals, metals alone, metals and hydrogen, etc., in the cracking operation. There is no doubt but that the rate of the reaction can be modified materially by catalytic agents. Exactly what the effect is quantitatively is not known yet. Undoubtedly we shall hear more about this in the future. Rittman is at present working on the effect of catalysers.

That sufficient time is not given for equilibrium to be reached in these reactions is shown by the optical activity of some of the products obtained. Kerosene fractions of most crudes show very little optical activity; while kerosene fractions of an Oklahoma oil heated at 100 pounds pressure show this activity according to Bacon and his collaborators, who are impressed with the fact that complete racemization has not occurred. Since these active molecules are stopping points in the readjustment of the atoms or groups set free in the cracking process it is indeed remarkable that we have optical activity at all. The effect of time should be given much consideration in studies of this nature for these are equilibrium reactions and they should complete themselves before analytical operations are applied. It is because of the possible saving of time required for equilibrium to establish itself, by means of catalysers that studies in this direction will be valuable.

Many of the ideas that have crystallized out of the mass of material on the subject of "cracking" appear to have been recognized by W. O. Snelling. In the Scientific American Supplement No. 2046, he describes some experiments which seem to emphasize the effect of the relative volume of the vapor phase. What effect his evidence will have on the questions of priority that undoubtedly will arise in patent considerations will be most interesting. Snelling has undoubtedly recognized the application of phase rule considerations, although he does not state the case as a formal one. In conclusion the writer believes that much valuable information can be obtained if a definite heavy hydrocarbon is "cracked" under the different conditions, rather than the very complex crudes. It will not be easy to get a pure body of this nature, and the analytical difficulties will be enormous. But problems as complex as this have been handled successfully. And with the commercial applications apparent, it is to be expected that the work will be undertaken.

It is announced in London that nearly $2,500,000 capital has been promised for the proposed British national dyestuff industry.

THE CHEMICAL SIMILARITIES OF HYDRAULIC CEMENTS, AND REFLECTIONS THEREON.*

By G. B. UPTON.

The hydraulic cements, of which "portland" is the most conspicuous example in common use, are chemically very complicated substances. In the manufacture of portland cement rocks containing lime (CaO), silica (SiO_2), and alumina (Al_2O_3) or substances approximately chemically equivalent to these, are ground, mixed in definite proportions, and then "burnt" in great kilns at very high temperature. The "clinker" coming from the kilns consists of chemical compounds of the component "radicals," CaO, SiO_2, and Al_2O_3. The clinker in its turn is ground to flour-like fineness, a small percentage of gypsum, $CaSO_4$, $2H_2O$, being added at this stage. In addition to CaO, SiO_2 and Al_2O_3 the rocks used as raw materials bring in magnesia (MgO) and iron oxide (Fe_2O_3), which may be impurities or may act like CaO and Al_2O_3.

The "natural" cements differ from portland in being ready mixed in the rock as mined, requiring only a slight burning. Chemically the natural cements have large amounts of MgO and little CaO, as compared with portland. In the purely artificial portland cement such large amounts of MgO cannot be used; the cement becomes "unsound."

It would be most convenient, and perhaps illuminating, to reduce the complicated actual chemical analyses to equivalent analyses of a simple character, which might show something of the chemical nature of the cements, or make possible an attack upon that problem. The first step in finding a reduced analysis is to eliminate the gypsum or other secondary material, to get to the actual composition of the cement as burnt. The MgO may be taken as acting chemically like CaO, and an equivalent amount of CaO computed for the MgO. Similarly Fe_2O_3 may be reduced to equivalent Al_2O_3. This reduces the cement to three components, CaO, SiO_2, and Al_2O_3. In this reduced analysis the CaO is a summation of actual CaO and CaO equivalent of MgO in the cement as burnt, while the Al_2O_3 similarly represents actual Al_2O_3 plus Al_2O_3 equivalent of the Fe_2O_3.

The molecular weights are as follows: $CaO = 56.1$; $Mg\ O = 40.4$; $Sio_2 = 60.4$; $Al_2O_3 = 102.2$; $Fe_3O_3 = 159.8$; $SO_3 = 80.0$; $H_2O = 18.0$. From these the reducing ratios may be worked out. CaO equivalent for the MgO is $\frac{56.1}{40.4} = 1.364$ times the actual MgO. The Al_2O_3 equivalent for the Fe_2O_3 is $\frac{102.2}{159.8} = 0.640$ times actual Fe_2O_3. Gypsum is CaO, SO_3, $2H_2O$. Hence the lime brought in with the SO_3 of the gypsum is $\frac{56.1}{80.0} = 0.689$ times the SO_3. The water brought in as water of crystallization of the gypsum is $\frac{2 \times 18.0}{80.0} = 0.450$ times the SO_3.

The following are examples of applications of the reduced analyses:

A. The average American portland cement of the year 1905, according to the U. S. Geological Survey, analyzed in per cents by weight CaO 62.73; MgO 1.99; SiO_2 22.46; Al_2O_3 7.49; Fe_2O_3 2.85; SO_3 1.46. In the cement as burnt the equivalent CaO was then $62.73 + 1.364 \times 1.99 - 0.689 \times 1.46 = 62.73 + 2.71 - 1.00 = 64.44$. The equivalent Al_2O_3 was $7.49 + 0.640 \times 2.85 = 9.31$. The equivalent amounts of CaO, SiO_2 and Al_2O_3 are 64.44, 22.56 and 9.31 respectively. These figures sum up to 96.31. Expanding the three items till they sum up to 100 per cent, the reduced analysis becomes CaO 66.93, SiO_2 23.41 and Al_2O_3 9.66.

B. The "iron ore" cement for the Panama Canal analyzes CaO 64.84; MgO 0.66; SiO_2 23.266; Al_2O_3 1.67; Fe_2O_3 8.20 SO_3 1.08. The equivalent CaO is $64.84 + 1.364 \times 0.66 - 0.689 \times 1.08 = 64.84 + 0.94 - 0.76 = 65.02$. The equivalent Al_2O_3 is $1.67 + 0.640 \times 8.20 = 1.67 + 5.26 = 7.93$. The sum of equivalent CaO, SiO_2 and Al_2O_3 is $65.02 + 23.26 + 7.93 = 96.21$. The reduced analysis, summing to 100 per cent, is CaO 67.60, SiO_2 24.17 and Al_2O_3 8.25.

C. An American natural cement analyzes CaO 33.70; MgO 20.94; SiO_2 24.30; Al_2O_3 7.22; Fe_2O_3 5.06. The equivalent CaO is $33.70 + 1.364 \times 20.94 = 33.70 + 39.70 = 63.40$. The equivalent Al_2O_3 is $7.22 + 0.640 \times 5.06 = 7.22 + 3.23 = 10.45$. The sum of equivalent CaO, SiO_2 and Al_2O_3 is $63.40 + 24.30 + 10.45 = 98.2$. The reduced analysis, summing to 100 per cent, is CaO 64.6, SiO_2 24.7, Al_2O_3 10.7.

For comparison the three analyses are now tabulated toegther. The reduced analyses are

	CaO	*SiO₂*	*Al₂O₃*
A = Average American Portland.	66.9	23.4	9.7
B = Iron ore Portland...........	67.6	24.2	8.3
C = American natural............	64.6	24.7	10.7

There is in these three reduced analyses of widely different materials an astonishing similarity. It may be said that this similarity is forced by our initial assuptions that we can change MgO to equivalent CaO, and Fe_2O_3 to equivalent Al_2O_3, by the ratios of the molecular weights. It seems a better view, however, to say that the similarity of the three analyses proves that our assumptions of equivalence are justified; that CaO and MgO, and likewise Al_2O_3 and Fe_2O_3, act similarly in the hydraulic cements, forming similar chemical compounds.

There is the objection that Portland cement cannot carry more than 4 or 5 per cent of MgO and remain sound. The answer to this is discovered in the recent work of the Geophysical Laboratory, which shows that it takes temperatures above 1500 C. or thereabouts to make MgO react with the other components of Portland in the few hours of burning of the clinker. Nature, with intimate mixing and plenty of time, has made MgO compounds in the rock of the "natural" cements which we cannot make in our furnaces. It seems, however, that these MgO compounds made by nature are of the same kind as the CaO compounds we make in the cement kilns.

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*From the Sibley Journal of Engineering.

With complete burning, finishing the possible chemical combinations, the hydraulic cements should consist of a mixture of the compounds tri-calcic silicate, 3 CaO, SiO_2, di-calcic silicate, 2 CaO, SiO_2, and tri-calcic aluminate, 3 CaO, Al_2O_3. If the burning is incomplete there will be less 3 CaO, SiO_2, with CaO free, and there may be still less 3 CaO, Al_2O_3 with CaO_3 and Al_2O_3 combined as 5 CaO, 3 Al_2O_3. In the latter case there would probably be no 3 CaO, SiO_2, at all.

The three cements given above as A, B, and C, if completely burnt, would agree in having in each case about ⅓ of their substance as 3CaO, Al_2O_3 and the other ⅔ as silicates of lime. A and B, the portlands, differ markedly from C, the natural, in the nature of their silicates. The natural cement has practically no tri-calcic silicate. The portlands have about half and half di-calcic and tri-calcic silicates; but if anything, less than half tri-calcic. This is in case of complete burning. If the burning is incomplete there is more di-calcic silicate, less tri-calcic, and *free lime*.

The natural cements will not stand the boiling test for soundness as the portlands do. But there is little complaint because of failures in service, in actual structures, of the natural cements; and the portlands do fail. Can the answer be in the tri-calcic silicate and the free lime of the portlands? If we lowered the lime content of portlands till they consisted of di-calcic silicate and tri-calcic aluminate (about 65 per cent CaO in the reduced analysis) would the portland cement be permanently sound and durable? That is a question that can only be answered by continued research.

CAMPHOR TREE IN FEDERATED MALAY STATES.

One of the interesting experiments that has had the close attention of the Director of Agriculture in the Federated Malay States is the effort to grow the Japanese camphor tree (*Cinnamomum camphora*), which was begun in 1912 at the experimental station at Kuala Lumpur, the capital of the Federated Malay States. The principal difficulty connected with growing the camphor tree has been getting a sufficient quantity of plants, as the seed very frequently fails to germinate. Another point that must be settled before success is attained is the number of times per year the bushes can be pruned for distillation. It is found that they recover much more slowly than was thought at one time.

A COMPARISON OF THE RELATIVE DRYING POWERS OF SULPHURIC ACID, CALCIUM CHLORIDE AND ALUMINUM TRIOXIDE WHEN USED IN ORDINARY SCHEIBLER DESICCATING JARS.[1]*

By J. W. MARDEN and VANNA ELLIOT.

In spite of the many objections put forward to $CaCl_2$ and H_2SO_4 for ordinary desiccating purposes, these substances are still quite generally used. Nearly every analyst knows from experience that if a perfectly dry sample of coal, for example, is placed in a desiccator containing $CaCl_2$, which has been used for some time, or concentrated H_2SO_4, the coal will increase in weight. When the desiccator is opened some moisture enters from the atmosphere, to be sure, but not enough to account for the increase in weight of the coal.

As compared to the wide use to which H_2SO_4 and $CaCl_2$ are put as drying agents for organic substances which cannot be heated, the literature on the subject is meager. The desiccating efficiency of several substances like $CaCl_2$, Na, fused NaOH, P_2O_5, etc., has been tried. Baxter and Warren[2] tried $CaBr_2$, $ZnBr_2$ and $ZnCl_2$ by passing moist air over them. They found that H_2SO_4 was more efficient than any of these. Johnson[3] has published a note on the use of Al_2O_3 as a desiccating agent in which it is claimed that Al_2O_3 is more effective than H_2SO_4 for removing moisture from air saturated with water vapor.

In the hope of suggesting a good substitute for the time-worn $CaCl_2$, if not for H_2SO_4, in ordinary desiccation, the present work was undertaken. Also, a series of experiments with H_2SO_4 has been run to show the effect of the concentration of the acid on drying certain substances, and it is hoped that the results will throw some light on the vagaries of H_2SO_4 as a desiccant. Many analysts seem in doubt regarding the total amount of moisture that is obtained by H_2SO_4 drying; some have the opinion that they get all but two or three-hundredths of one per cent in most cases, while others think that they obtain very much less than that percentage of moisture. At best, any drying method with H_2SO_4 can be only an arbitrary one. Since this is an old subject, most of the experimental work for this paper is given in abstract.

Many experiments have shown that from certain substances all of the moisture cannot be obtained by the ordinary H_2SO_4 drying method at 25° C. A sample of pure sugar syrup, for example, containing 49.89 per cent moisture, mixed with ten times its weight of sand, yields an average of about 48.17 per cent moisture. With maple syrup, even with vacuum, the same condition is observed. The percentage of moisture obtained by H_2SO_4 drying is less than that obtained by the refractive index or by heating at 100° C. This behavior of sugar, although somewhat exaggerated, is typical of the behavoir of other substances. The water-vapor pressure of some materials still containing residual moisture is as low as that of the H_2SO_4 over which they have been dried. It has been shown that considerable amounts of H_2SO_4 distil off in vacuum, and for this reason Gore[4] suggests the use of CaO for high vacuums. By graphic interpolation, concentrated (95%) H_2SO_4 has a vapor pressure of about 0.03 mm. at 25° C.

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*From the Journal of Industrial and Engineering Chemistry.

[1] This work was started in the laboratory of the South Dakota State Food and Drug Department.

[2] J. Am. Chem. Soc., 33 (1911), 340.

[3] Ibid., 34 (1912), 912.

According to Thorpe[5] the speed of drying is hastened but no more moisture is obtained by the use of vacuum. In a series of trials with cheese, syrup, coffee, etc., using both H_2SO_4 and $CaCl_2$, slightly more moisture was obtained with vacuum than without.

In one instance it was much as 0.7 per cent and in other cases quite small.

The effect of a fairly large variation in the concentration of H_2SO_4 changes the total amount of moisture removed from some substances very slightly; in other cases, however, the change is marked. Table I shows the results obtained with flour, cane-sugar syrup and cheese dried to constant weight over various concentrations of H_2SO_4. Each sample for each concentration was dried in an individual desiccator:

TABLE I.—EFFECT OF CONCENTRATION ON DRYING POWER OF H_2SO_4.
Atmospheric Pressure and Laboratory Temperature.
Total Time of Drying: About Three Weeks.

Per cent H_2SO_4.	Vapor Pressure mm. of Hg (approximate).	Per cent Water in White Flour.	Cane Syrup.	Cheese.
95	(0.03)?	12.48	48.28	26.51
84.8	0.18	12.28	48.25	26.10
78.3	0.8	10.04	48.27	25.58
65.6	2.7	7.22	48.10	24.88
62.6	3.5	2.89	47.97	23.47
37.0	15.0	0.10	47.30	21.18
29.6	17.5	.....	34.70	.....
21.9	20.0	.....	22.01	.....
15.2	21.0	.....	0.29	.....
7.0	22.5	.....	49.4	(increase in weight)
Per cent moisture found by drying at 100° C. to constant weight..		11.85	49.78	26.65
Polariscope		.....	49.89	.....
100 per cent(*a*) H_2SO_4		12.55	48.28	26.65

(*a*) Values obtained by plotting percentage moisture against percentage H_2SO_4.

It will be seen from Table I that cane syrup could be dried about as well, although, as laboratory experience showed, not as quickly, over 75 per cent as over 100 per cent H_2SO_4. With cheese the percentage of moisture obtained over 100 per cent H_2SO_4 is about the same as that by drying to constant weight at 100° C. Flour shows another example of the increase in weight of some materials on heating, due to a certain amount of oxidation. Skertchly[6] has pointed out inconsistencies of this kind which he found while drying biscuits.

As has been suggested by several authors, exposing a substance over varying concentrations of H_2SO_4 and finding the concentration at which it neither gains nor loses weight indicates the concentration of H_2SO_4 which has the same vapor pressure as the material. In this way flour has a vapor pressure of about 15.0 mm. and cane-sugar syrup of about 21.0 mm.

Hempel[7] has shown that the rate at which substances dry depends upon the rate which water vapor is transferred. Since air saturated with water vapor is less dense than unsaturated air, Hempel puts the H_2SO_4 in the upper part of the desiccating jar. Similarly, if air currents can be formed in the jar, the drying will go much faster. To show this point, samples of maple syrup were dried over 95 per cent H_2SO_4 at room temperature in two desiccators; in one a small motor was introduced and the air stirred vigorously during the experiment. In one and one-half hours as much moisture was removed with stirring as was removed without stirring in six hours.

Several portions of Al_2O_3 were prepared for comparison with the other desiccants. The Al_2O_3 used in the preliminary trials was prepared from "technical" $Al_2(SO_4)_3$ by dissolving the salt in water and precipitating the $Al(OH)_3$ with NH_4OH. The aluminum hydroxide was filtered off and dehydrated in the glass tube of a combustion furnace with the smoky flame. The Al_2O_3 employed in the later experiments was made in the same way, except that "C. P." $Al_2(SO_4)_3$ was used in the preparation and the $Al(OH)_3$ was washed many times to remove any impurity which might lead to erroneous results.

Preliminary experiments comparing Al_2O_3 with $CaCl_2$ showed that in nine days at laboratory temperature and pressure, a sample of coffee yielded 0.2 per cent more moisture over Al_2O_3 than over $CaCl_2$. In the same length of time a sample of sugar yielded the same weight of moisture over either. The percentage of moisture in this case, however, was very low. Trials were made, also, by placing weighed dishes of Al_2O_3 over H_2SO_4 and H_2SO_4 over Al_2O_3 to see which would increase in weight more rapidly. The moisture introduced by opening the desiccator was enough to vitiate the results somewhat, but the Al_2O_3 increased in weight faster than the H_2SO_4. The following table shows the percentage of moisture obtained with three common materials dried over the three desiccants and kept in a thermostat at 25° C. Each percentage shown is the average result of duplicate experiments in in-

TABLE II.—PERCENTAGE OF MOISTURE BY DIFFERENT DESSICANTS.

Substance.	Flour.			$CuSO_4.5H_2O$			Coffee.	
Time, Days.	Al_2O_3 per cent.	H_2SO_4 95 per cent.	$CaCl_2$ per cent.	Al_2O_3 per cent.	H_2SO_4 95 per cent.	$CaCl_2$ per cent.	Al_2O_3	$CaCl_2$
1	8.42	8.42	8.47	14.12	15.08	15.22	1.31	1.17
2	9.51	9.56	9.21	18.76	19.47	16.84	1.98	1.82
3	10.30	10.33	10.06	23.73	25.51	21.31	2.66	2.38
4	10.67	10.61	10.35	28.11	28.74	25.40	3.11	2.92
5	11.08	10.96	10.62	29.36	29.46	28.77	3.30	3.11
6	11.21	11.13	10.75	29.43	29.45	29.32	3.44	3.22
7	11.46	11.33	10.96	29.53	29.54	29.42	3.54	3.32
8	.....	.....	.....	.....	.....	.....	3.66	3.46
10	.....	.....	.....	29.53	29.54	29.42	....	....
11	11.75	11.64	11.15	.....	.....	.....	....	3.46
13	11.75	11.64	11.15	29.53	29.54	29.42	....	....

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[4] J. Biol. Chem., 15, 259-61.

[5] "Dictionary of Applied Chemistry," Vol. II, p. 210 (1912). Longmans, Green & Co.

[6] J. Soc. Chem. Ind., Jan., 1913.

[7] Ber., 23 (1890), 3566.

dividual desiccators over the same weight of desiccant.

The time values in Table II are given roughly in days, which intervals are close enough to show the points in question. Some of the moisture in the blue vitriol was lost in grinding the sample.

The work in Table II was repeated in vacuum desiccators at a pressure of about one-tenth atmosphere and at laboratory temperatures. As before, three substances, flour, blue vitriol and tea, were dried over the three desiccants. Although there was some difficulty in obtaining desiccating jars with the same power for "holding" the vacuum, the average results were in the same order as in the above table. For small amounts of moisture Al_2O_3 appears to be somewhat superior to either H_2SO_4 or $CaCl_2$, when used in this way, while with $CuSO_4.5H_2O$, which has a larger percentage of moisture, there seems to be but little choice between Al_2O_3 and 95 per cent H_2SO_4. $CaCl_2$ seems to be inferior to either of the others. It is possible that H_2SO_4 methods of drying may give better results when the acid has frequent agitation, and when two or three charges of fresh acid are added during a determination. Al_2O_3 has the further advantages that one need not guard against slopping, burns, etc., as when using H_2SO_4 and that this oxide can be reheated when it becomes saturated with water and used again and again.

NEW METHOD OF EXTRACTING LEMON OIL.

U. S. Consul Joseph Emerson Haven, Catania, Italy, reports that a new chemical process has just been invented by Prof. Liotta, a resident of his district, which is thought will revolutionize the lemon-oil industry. Up to the present all chemical processes have caused changes in the properties and smell of the essence, but the new process is said not to affect the oil in any way.

The new process is carried out as follows: The lemons are mashed in a large receptacle, and an acid, the nature of which is kept secret, is added. This acid causes the essential oil to separate and rise to the surface, from which it is drawn off. A chemical reagent is then added to the acid mixture that liberates the acid and permits its recovery. The residue, consisting of lemon juice, pulp and peel, and foreign matter, is then sold to citrate manufacturers.

The new process will save about 2½ per cent more oil than the old hand process. The cost of extraction is only 2.3 cents per 1,000 lemons and the process requires only 22 minutes. It is thought that this time will be reduced to 12 minutes when the process has been further perfected and under commercial operation.

The present method of extracting essential oils from citrus fruits in eastern Sicily and Calabria is known as the sponge process. The fruit is first soaked in water for a short period and the peel is then removed in three sections and each section pressed by hand into a sponge. The sponge absorbs the oil that is liberated from the peel by the pressure, as well as a certain amount of water.

From time to time the sponge is squeezed into a bowl, which when filled is allowed to stand until the essential oil rises to the surface. The oil is then removed and filtered. This is the most primitive process and survives only because of cheap labor. The cost of extraction under this process is 4.50 lire ($0.868) per 1,000 lemons.

In northern Italy and southern France another method, known as the "ecuelle process," is employed, the fruit being placed in a saucer-shaped vessel 10 inches in diameter, which is lined up with small quarter-inch spikes. A tube at the base allows the oil to fall into a vessel below. The surface of the fruit peel is bruised by contact with the spikes when the ecuelle is given a swift, rotary motion, and the oil is liberated and descends by gravity into the container beneath.

STANDARD FOR CONDENSED MILK.

Condensed or evaporated milk should be made from the whole, fresh, clean milk produced by the complete milking of healthy cows, and contain a definite amount of nutritive materials as indicated by milk fat and total solids, according to a food inspection decision issued by the United States Department of Agriculture. The definition embodied in the decision will guide the officials of the Department in the enforcement of the Food and Drugs Act. The product, to be in accordance with the definition, must contain not less than 25.5 per cent of total solids and not less than 7.8 per cent of milk fat.

The total solids include all the substances in the condensed or evaporated milk except moisture, and are, therefore, an index of the actual food value of the product. The department officials are of the opinion that by fixing a minimum below which neither the total solids nor milk fat may fall a condensed milk of high nutritive value is insured. It is stated that no tolerances whatsoever below the quantities fixed in the decision will be permitted.

The definition also requires that the milk must be from cows properly fed and kept, and is intended to prevent the sale of condensed milk made from milk from cows fed upon unwholesome feeding stuffs, such as swill and brewery slop, or which have been kept under such insanitary or otherwise unfavorable conditions as might impair the quality of the milk.

The definition for condensed milk as embodied in the food inspection decision is the same as the definition and standard recommended by a joint committee from certain state and national organizations having to do with the enforcement of laws relating to foods. The organizations represented on the Joint Committee on Definitions and Standards are the American Association of Dairy, Food, and Drug Officials, the Association of Official Agricultural Chemists, and the United States Department of Agriculture.

METALLURGY.

VANADIUM IN GERMAN ORES.*

The presence of vanadium in certain iron ores of Germany, and details regarding its behavior during the ordinary metallurgical operations, are mentioned in an interesting paper by L. Blum, in a recent issue of Stahl and Eisen. He is chief chemist at the large new plant at Esch, and his attention was directed to the matter because of the difficulty experienced in correctly estimating the iron in basic Bessemer slags, a difficulty caused by the presence of vanadium. The ordinary Reinhardt process on six of these slags gave an average of 10.46 per cent iron. Careful gravimetric results, carried out so as to separate the vanadium, only gave 9.54 per cent iron. Mr. Blum then recommends methods of analysis. In very brief outline they are that in one sample the iron and vanadium be titrated together with potassium permanganate, and in another the vanadium alone. The difference gives the permanganate used on the iron, from which the percentage can be calculated. Results obtained in this way gave 9.51 per cent iron, agreeing well with the 9.54 per cent obtained by gravimetric determination.

These results caused Mr. Blum to investigate the metallurgical side of the question. No vanadium could be found in the ash of the coke used in the blast furnace, in the Poti ore used as a flux with the Minette ore, nor in the lime used as a flux in the Bessemer process. The vanadium found in the Bessemer slags can only come, therefore, from the Minette ore. Analyses of eleven ores are given in the following table:

ANALYSES OF MINETTE ORES.

No.	Mine.	Iron, per cent.	Vanadium, per cent.	Corresponding Vanadic Acid, per cent.
1.	Bouvenberg von Redingen	37.49	0.102	0.182
2.	Vereinigte Huttenwerke von Belvaux	36.75	0.102	0.182
3.	Victor at Hayingen	29.64	0.071	0.126
4.	Lallingerberg at Eich	25.63	0.095	0.169
5.	Yellow Minette, Langengrund at Rumelingen	31.86	0.102	0.182
6.	Brommeschberg at Tetingen	29.41	0.088	0.156
7.	Esch Hoehl, red silicious layer	29.00	0.092	0.163
8.	Esch Hoehl, red lime layer	27.44	0.075	0.133
9.	Esch Hoehl, grey layer	30.52	0.068	0.121
10.	Esch Hoehl, brown layer	42.23	0.095	0.169
11.	Esch Hoehl, black layer	41.34	0.109	0.194

The five last analyses, Nos. 7 to 11, give ores from one mine arranged according to their geological age, the youngest being given first and the oldest last. There is no great difference in the vanadium contents.

The first product of this ore, basic Bessemer iron with about 0.4 per cent silicon, 1.2 per cent manganese, 1.8 per cent phosphorus, and 0.06 per cent sulphur, shows that the vanadium partly enters the iron and is partly slagged off. The iron from four different casts gave:

Test 1	0.203 per cent vanadium
Test 2	0.203 per cent vanadium
Test 3	0.155 per cent vanadium
Test 4	0.163 per cent vanadium
Average	0.181 per cent vanadium

The blast furnace slag gave:

Test 1	0.139 per cent vanadium
Test 2	0.144 per cent vanadium
Test 3	0.105 per cent vanadium
Test 4	0.107 per cent vanadium
Test 5	0.109 per cent vanadium
Test 6	0.120 per cent vanadium
Average	0.121 per cent vanadium

The vanadium in the ore behaves like manganese in the blast furnace, in that according as the furnace works hotter or colder, a more or less large part of the vanadic acid is reduced or slagged off.

The vanadium in the iron is easily oxidized and slagged. On the way from the furnace to the pig-iron mixer the small amount of slag that is formed shows 1.19 per cent vanadium, corresponding to 2.11 per cent vanadic acid. The mixer slag also shows that more has been oxidized. An average of two samples gave 0.370 per cent vanadium. Another test, which was an average sample of a week's production, gave 0.50 per cent vanadium, corresponding to 0.908 per cent vanadic acid. After these losses the iron to be blown gives the following results:

Test 1	0.149 per cent vanadium
Test 2	0.176 per cent vanadium
Test 3	0.149 per cent vanadium
Average	0.158 per cent vanadium

This is practically all oxidized during blowing in the converter, being found in the basic Bessemer slag as vanadic acid. The steel from two heats showed 0.013 and 0.007 per cent vanadium, an average of only 0.01 per cent. The average of six different days' slag analyses gave 0.87 per cent vanadium, equal to 1.59 per cent vanadic acid; and another average of four days' analyses gave 0.70 per cent vanadium, equal to 1.24 vanadic acid.

The British oil-seed crushing industry has not met with the curtailment which the country's foreign trade statistics show has been the case with many other British industries. The imports of oil seeds and nuts into the United Kingdom in 1913 had a value of $77,000,000, and the same in 1914. There was a drop of about $7,000,000 in flaxseed, but a compensating gain in "nuts and kernels"—a large part of which was evidently in copra or the dried meat of the cocoanut.

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*From The Iron Age.

TITANIUM AND TITANIFEROUS ORES.*

By PAUL H. BERGGREEN, M. E.†

Although the supplies of iron ore that are available in the United States are still to be measured by millions of tons, yet the approaching exhaustion of high grade deposits stands as a fact and must necessarily confront the American ironmasters with the problem of efficient reduction of lower-grade ore.

Magnetite containing a high percentage of titanium is of particular interest, as from time to time the discovery of enormous bodies of titaniferous ores has been reported, and the proper utilization of such deposits would postpone the arrival of an iron-ore famine almost indefinitely.

The term "titaniferous magnetite" is used to designate those magnetic ores of iron that carry more than 2 or 3 per cent of titanium. Deposits of this kind have until recently been practically worthless, as already iron ores containing over 1 per cent of titanium are regarded so troublesome to smelt that they are not accepted by the smelters. The existing prejudice against the use of ores carrying more than 1 per cent of titanium is based chiefly on the belief that the ores require an undue amount of fuel to reduce them, and that they cause the accumulation of infusible titanium compounds that ultimately choke the furnace.

A historical review of the use of titaniferous iron ores shows that their use has gradually declined. In the early days of the Catalan forge and small charcoal furnaces it did not matter much how large a quantity of charcoal a certain charge required, and therefore it did not seem to make any particular difference whether an ore was titaniferous or not. Many titaniferous deposits were then worked and smelted without difficulty. Later, as the furnaces increased in size, and the amount of fuel required became an important economic factor in the industry, these deposits were abandoned. However, because such deposits are so numerous and so large, and the ores nearly always so low in phosphorus and sulphur, they have never ceased to attract attention and many experiments have been conducted looking to a means of solving the problem of their utilization.

This problem has been attacked along two lines—first, the use of milling methods, involving the elimination of titanium from the ores, so as to make possible their smelting in the usual way; second, by the use of metallurgical processes, involving the direct reduction of the ores. The former method constitutes a mechanical process, the latter a chemical process.

As titanium occurs in the ore in the form of non-magnetic ilmenite, the first process consists of a separation of the mechanically mixed magnetite and ilmenite by a magnetic concentration after fine crushing. Such treatments have given but little success, and recent investigations have disclosed the cause of this to be the presence of titanium in the magnetite itself in a form not separable from the magnetite by any known mechanical process. Consequently the problem of utilizing titaniferous ores should involve the application of chemical rather than mechanical methods.

The thorough experiments by Rossi in the early nineties proved the possibility of eliminating titanium through the formation of relatively fluid slags consisting of complex titano-silicates, and although other prominent investigators have continued his work along these lines, there seems to be no inclination on the part of the iron masters to adopt furnace practice to these conditions.

While already Bergman in 1770 in his studies on iron-alloys points out to us the peculiar properties of iron containing small quantities of titanium, so little was done in research on this subject, that Leon Guillet only nine years ago said: "Titanium is of interest only from the point of view of the elimination of Nitrogen."

J. T. Singewald has made a thorough investigation as to the possibilities of utilizing the various deposits in this country of titaniferous ore. He has studied in detail the physical structure and chemical composition of the ores in their relation to the problem of utilization, and has concluded that it is practicable to use small proportions of the concentrates from a magnetic separation of the titaniferous ores in blast-furnace mixtures with little change in present methods and without danger of choking a furnace.

O. Simmersbach describes the successful smelting of titaniferous iron ores in ordinary blast-furnaces. The ore contained about 12 per cent titanium and was mixed with ordinary magnetite in the proportions 1:11 and 1:5. No difficulties were encountered as long as the titanic acid in the slag was below 3 per cent.

Important results of similar investigations have been published by E. F. Cone. This series of tests is probably the largest and most extensive of the kind ever undertaken, and has excited wide attention amongst the blast-furnace men of the country by proving the possibility of successful smelting into a marketable pig-iron of the vast deposits of high-grade titaniferous ores of the Sanford Hill district in New York state.

The introduction of the electric furnace has opened great possibilities, and there is a confident feeling in many quarters that herein lies the hope of the ultimate utilization of titaniferous low-grade iron ore. The electric smelting of such ores is still in its infancy, but the direct derivation of ferro-titanium by electric arc smelting has greatly facilitated the study of the important influence of titanium upon the characteristics and properties of irons and steels.

Mossan and Rossi started in 1892 and 1902, respectively, successful attempts to reduce titaniferous iron ore in the electric furnace, either with carbon or with assistance of molten aluminum, which was already known to facilitate the reduction of the metal from

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*From Sibley Journal of Engineering.
†Librarian in Sibley College.

its ore. Since 1907, when ferro-titanium was first employed in the trade, its use has increased very rapidly, and the reports and investigations published on the effect of titanium upon iron and steel are numerous. M. H. Wickhorst for instance has given a very extensive report on titanium in bessemer ingots and rails. He recommends an addition of 0.10 per cent. The Titanium Alloy Mfg. Company, who is the owner of the more important patents in this line, is issuing regular Rail Report Bulletins containing complete descriptions of tests of open-hearth rail-steel as to homogeneity, segregation, ductility, impact and dynamic resistance.

A good many experiments have been made to ascertain the effect of titanium upon cast iron, and a tabulated comparison between results obtained by various investigators have been published. The effect of titanium on the magnetic properties of iron has been subjected to investigation by K. P. Applegate. He finds that small amounts of pure titanium increase the permeability of pure Swedish charcoal iron and decrease the hysteresis loss.

These few examples should indicate the great interest aroused lately as to the future possibilities of titaniferous iron ores and to titanium-treated iron and steel. The scepticism which undoubtedly still exists among our smelters, will gradually give way to a firm belief in the advantages of utilizing the enormous resources of low-grade iron ore containing a high percentage of titanium. The actual nature of the titaniferous ore is but little understood, and our knowledge of the chemical conditions in the blast-furnace and the electric furnace is still so limited as to warrant continued research and investigation.

CHINESE ANTIMONY FOR UNITED STATES.

A Chinese mining and smelting company has opened an office in New York for the sale of antimony in the United States. Through the New York office of the Bureau of Foreign and Domestic Commerce it was put in touch with a concern which has already purchased $40,000 worth of its antimony.

It is interesting to note that the bulk of the United States annual purchase of about 15,000,000 pounds of antimony comes from China. The following statistics for recent fiscal years ended June 30 show direct importations from China:

From—	1911.	1912	1913.	1914.
All countries:				
Pounds	10,036,401	13,919,164	19,584,624	14,263,629
Value	$541,588	$693,218	$1,134,467	$696,362
China and Hongkong:				
Pounds	3,185,453	4,646,831	6,909,995	4,300,892
Value	$131,755	$177,663	$286,455	$190,737

England is credited in the United States customs returns as furnishing nearly half of the imports of antimony, but it is understood that most of this is from China. The desire of Chinese miners is to sell their antimony direct to American buyers.

BRAZILIAN MONAZITE.

It would seem that most of the very limited supply of extracted monazite sand lies at present in Europe. So far as can be ascertained, it does not exceed 8,000 to 9,000 tons, obtained chiefly from Brazil and British India. The world's supply of monazite appears to come from a limited number of sources. After the American production from Burke County, N. C., which, it is said, never leaves the United States, there appear to be only the more or less mysterious deposits of the Ural Mountains in Russia; those of British West Africa, of whose workings little seems to be known; a hint of deposits in one of the West Indian Islands; the British Indian deposits at Travancore; and those of Brazil. The following account of the last mentioned deposits is taken from a report of Consul General A. L. M. Gottschalk, Rio de Janeiro, in the Daily Commerce Report:

Analysis and Uses of Brazilian Monazite Sand.—The following analysis of Brazilian monazite sand was furnished by Mr. F. H. Lee, associated with the Geological Service of the Brazilian Government: Phosphoric acid (P_2O_5), 29.28, cerium oxide (Ce_2O_3), 31.28; lanthanum oxide, (La_2O_3) and didymium oxide (Di_2O_3), 30.88; silica (SiO_2), 1.40; thoria (ThO_2), 6.49; loss on ignition, 0.20; total, 99.53. Mr. Lee states that no complete analysis of the product as found in this country is known to him; and that the mean thorium-oxide content of the product regularly marketed from the only sources thus far found to be commercially payable, ranges from 5.75 to 7.1 pei cent. The product marketed here carries about 92 per cent pure monazite, and runs from 6.2 to 6.4 per cent of thoria.

Monazite has been described as a phosphate of ceria, found in the so-called monazite sands, which contain this (yellow) phosphate, in combination with quartz, ilmenite (titanic iron), garnet (white), zircon, etc., and salts of various rare earths, such as erbia and terbia. No commercial use had ever been found for any of its components until it was established that the chemical thoria in certain of its forms possesses the peculiar property of transforming heat into light waves. It is as the source of thoria that monazite sands have industrial value, nitrate of thoria being the fluid into which gas mantles are dipped.

General Character of the Brazilian Deposits.—The known deposits of Brazil seem to lie in a coastal strip running south from Maranhao to the northern part of the state of Rio de Janeiro and in some river beds in the interior of the Republic. The coastal strip consists of Cretaceous to Quaternary beds, the product of the decomposition through the ages of the granite rocks upon which these beds border. They are the result of the action of wind and water concentrating the sand and leaving behind only its heaviest particles.

The deposits of the interior appear to lie entirely in the sandy beds of rivers. It is the general opinion that these beds are thin, scattered, and spread over too much ground to make the product easily transportable; and it should be borne in mind that transportation charges from the interior are very high. Almost all the larger rivers of the states of Minas Geraes, Espirito Santo, and Rio de Janeiro show some traces of these deposits, but their working is regarded by local expert opinion as impracticable.

There are also certain deposits of zircon oxide in the interior, which, as this mineral contains thoria, may some day be of interest industrially. From Dr. Orville A. Derby, the American scientist who for many years has been at the head of the Brazilian Geologic and Mineralogical Service (a bureau of the Brazilian Ministry of Agriculture), it is learned that no official examination of these deposits has been made, although it is certain that some scores, and perhaps hundreds, of tons of the ores have been shipped to Germany. Dr. Derby also states that a mineral known as baddelelyite, consisting of almost pure zircon oxide, occurs at various points over a considerable area in the Caldas district on the boundary of the states of Sao Paulo and Minas Geraes. The pure mineral cannot be counted on for any length of time, but mixed mineral, running from 90 down to 75 per cent, may perhaps be counted on. The deposits appear to be in the hands of private persons.

Competent persons who have mined the river sands of the interior of the state of Pao Paulo state that these were found to contain only 2 per cent of monazite, and that work was therefore abandoned. The river sands of the state of Espirito Santo are being worked by two companies of which little is known except that one is said to be financed by a diamond merchant of Paris.

Location of Most Important Monazite Beds—New Mining Law.—It appears almost impossible to obtain any more definite information, the persons concerned being almost invariably unwilling to disclose their sources of supply, perhaps because most of the beds of monazite sand will not renew themselves by the denudation of coast strata. The following places, however, have been mentioned as the locations of deposits of widely varying value: Praia Massanduba, near Cape Frio, deposits of titaniferous iron containing some monazite; Macaha, 45 miles farther north, a small deposit; at the foot of the Cliffs of Siry, 30 miles north of the southern frontier of the State of Espirito Santo, a reputedly rich bed; at Maratayso Praia, 2 miles farther north, a poor bed; at the foot of Mount Aga, at Piuma, just south of Benevente, two beds not far apart; at Ubu, 4 miles north of Benevente, a better deposit; 2 miles north, at Maimba, and 2 miles farther north, at Miahype, Federal beds with extensive private marginal deposits. Miahype is considered by some persons one of the richest beds in Brazil. Four miles north of this come the southernmost of the Guarapary beds—Rastinga, Canto de Riacho, Praia de Diogo, etc. Nothing occurs for 15 miles northward till Ponto da Fructa and Victoria. Eighteen miles north of Victoria is a deposit at Nova Almeida, and 20 miles farther one at Regencia, described as particularly large. Seventy miles farther north are the Sao Matheus beds. It is said that certain beds still farther north—those of Prado, in the State of Bahia—are constantly being renewed by the wave action of extremely high tides beating upon the clay cliffs. Two other beds in the State of Bahia are mentioned—one at the mouth of the Cahy River and another just north of the River Carahyba. It is said that neither is important.

The new Brazilian mining law, promulgated on January 7, 1915, under its article 42 increases the privileges of small placer miners. This may possibly have some effect on developing, or increasing interest in, the scattered river-bed deposits of monazite sand in the interior. A translation of this new mining law is in course of preparation and will probably be printed within a few weeks. Persons desiring to obtain copies should address the Serviço de Informaçoes, Ministerio da Agricultura, Rio de Janeiro, Brazil.

Fluctuation in Monazite Sand Exports—Decline in Prices.—The exports of monazite sand from Brazil from 1905 to 1913 (no later figures being obtainable) and the principal countries of destination for the last four years mentioned are shown in the following table:

Years and countries.	Metric tons.	Value.
1905	....	$485,184
1906	....	480,843
1908	....	157,475
1909	....	708,092
1910	5,437	631,251
To United States	1,100	130,650
To Germany	2,636	303,953
To France	1,691	195,466
1911	3,686	539,299
To United States	700	101,352
To Germany	1,890	280,996
To France	1,096	156,961
1912	3,397	527,268
To United States	600	93,197
To Germany	1,852	291,467
To France	945	142,604
1913	1,437	186,478
To United States	400	51,905
To Germany	256	33,181
To France	778	101,003

It may be observed that the figures show a drop from $480,000 in 1906 to $157,475 in 1908, and that no figures are given for 1907. Further, it may be noted that in 1909 the figures jumped from the $157,475 of the preceding year to $708,092. After that they seemed to resume what might be termed a normal gauge until 1913. There is every indication that these fluctuations have been caused by speculators, one of whom realizing the smallness of the world's supply and believing that the demand was growing tried to fill Europe with stocks of the product in order to control future prices. The price of the commodity has dropped since 1907, but it is difficult to obtain authoritative information on the subject.

ENGLISH PRODUCTION OF CYANIDES.

Cyanides of potash and sodium are produced in large quantities in the United Kingdom, but the production of cyanide of sodium is largely outstripping that of cyanide of potassium, owing, it is stated, to the fact that the former can be more economically produced than the latter.

The comparative prices of the two cyanides during the first six months of 1914 and on Feb. 12, 1915, according to the Daily Commerce Reports, are as follows: Carbonate of sodium, first six months 1914, 14 cts. per pound; Feb. 12, 1915, 17 cts. per pound. Cyanide of potassium, first six months 1914, 15 cts. per pound; Feb. 12, 1915, 30 to 36 cts. per pound.

The greater relative increase in the price of cyanide of potassium is accounted for by the increased cost of potash. Carbonate of potash during the first six months of 1914 sold at $68 per ton, whereas the current price is $170.23 per ton.

The returns of the British Board of Trade do not distinguish separately the quantities and values of potassium cyanide and sodium cyanide exported from the United Kingdom, the two cyanides being combined in the returns. In 1913 the quantities and values of the cyanides of potassium and sodium exported from the United Kingdom were as follows, the countries of destination being indicated (hundredweight = 112 lbs.):

Destination.	Hundredweight.	Value.
Portuguese East Africa	13,058	$257,053
Japan	7,680	127,712
United States	3,283	59,946
Mexico	14,300	287,785
Brazil	3,257	63,459
Other foreign countries	7,985	137,829
Total foreign countries	49,563	$993,784
Transvaal	27,765	557,482
British India	3,797	76,827
Australia	33,348	681,485
New Zealand	6,375	130,281
Canada	8,147	132,383
Other British possessions	11,477	223,854
Total British possessions	90,909	$1,802,313
Grand total	140,472	$2,736,097

There are no imports of cyanide into the United Kingdom.

From the American consul at Glasgow it has been ascertained that the largest individual cyanide factory in the world is located in that city and is now being worked at its full capacity. It is furnishing the requirements of the Transvaal and also makes occasional shipments to the United States. The manager of the company states that since Jan. 1, 1915, the value of the shipments to the United States has amounted to $7,715. The same company has exported in the past to Mexico, but at present that country is not importing. The manager of the company also stated to the consul at Glasgow that Great Britain was able to supply all British requirements and to export to other countries.

AN INVESTIGATION OF THE EXTRACTION OF POTASH FROM FELDSPAR.*

ELWIN H. QUINNEY.

The vast amount of potash locked up in feldspars and feldspathic rocks and the great demand which has recently arisen for an American supply of potash in available form for agriculture, has stimulated not only a search for new deposits but has caused many of the best chemists of our country to search for a method by which this potash can be made available on a commercial scale. The natural silicates commercially available as sources of potash are chiefly orthoclase and leucite. Both of these minerals are potassium aluminum silicates. The theoretical formula for orthoclase is $K_2O\ Al_2O_3\ 6SiO_2$ and for leucite $K_2O\ Al_2O_3\ 4SiO_2$. The principal sodium feldspar, albite, has the theoretical formula $Na_2O\ Al_2O_3\ 6SiO_2$. It is well known that these feldspars run into and substitute each other in various proportions, so that different products will vary widely in respect to their soda, potash and aluminum contents. Iron is often found associated with these minerals.

The following investigation was carried on at the South Dakota State School of Mines with the supervision and assistance of Professor M. F. Coolbaugh. The rock used was a crystalline orthoclase feldspar which contained 9.02 per cent K_2O, 21.30 per cent Al_2O_3, 1.60 per cent Fe_2O_3 and 62.10 per cent SiO_2.

THE GYPSUM METHOD.

The sample of feldspar was heated with an excess of gypsum. After leaching with water an appreciable amount of potassium was found in the filtrate, and the quantitative investigation was begun.

A series of experiments with feldspar and gypsum heated to a high temperature gave the following results. (See Table I.)

Although a very satisfactory extraction by this method was obtained it can readily be seen that it could never be made a commercial success because of the great decrease in per cent of potash in the final product.

The law of mass action explains this large amount of gypsum necessary to get the extraction. The reaction which probably takes place is as follows: $K_2O\ Al_2O_3\ 6SiO_2 + 6CaSO_4 = K_2SO_4 + Al_2O_3 + 3SiO_2 + 3Ca_2SiO_4 + 5SO_3$. The theoretical amount of $CaSO_4$ required to complete the reaction is 0.735 grams, when 0.5 grams of feldspar is taken, or about one part feldspar to one and one-half parts $CaSO_4$. But as shown above (Table I) the reaction is evidently not completed with two parts of $CaSO_4$. However, when the mass of $CaSO_4$ is increased to eight parts the reaction is nearly completed.

SALT AND SULPHURIC ACID METHOD.

The problem then seemed to be to find something that would unite more quickly with the feldspar and not be influenced by the law of mass action.

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*From Pahasapa Quarterly.

Since chlorine unites very readily with potassium it was reasoned that if this element could be liberated in a mixture it might solve the problem. Naturally the cheapest possible materials were selected from which to make the chlorine, namely, salt and sulphuric acid. The method employed was to heat the feldspar with a certain quantity of salt and sulphuric acid. A large number of tests were run according to this method before anything like uniform results were obtained. The following is a tabulation of the results. (See Table II.)

As shown above a few tests were made at very low temperatures. At first these looked promising for a decided reaction of some sort had taken place, the whole mass turning to a white cake. When the temperature was increased a little, as in No. 3, the iron seemed all to go to the oxide, giving the mass a reddish tinge when cold. The extraction, however, was very low and proved that the change was due to the salt and sulphuric acid alone and not to any reaction with the feldspar. By keeping the amount of salt constant and varying the temperature and *vice versa* it was discovered that both the amount of salt and the temperature affected the reaction. The probable reaction is as follows: $2NaCl + 2H_2SO_4 + K_2O\ Al_2O_3\ 6SiO_2 = Na_2SO_4 + K_2SO_4 + Al_2O_3 + 2HCl + H_2O + 6SiO_2$.

Assuming that the reaction of the potassium and chlorine would go to completion before the aluminum was attacked, and since the amount of chlorine necessary is directly proportional to the salt, it was figured that the amount of salt necessary to unite with the potassium would be about one part to two parts feldspar. This proportion even with the highest temperature gave less than 50 per cent extraction. By increasing the mass of salt somewhat a trifle better results were obtained, but still too low. The amount of salt necessary to unite with both the potassium and aluminum was then added. This was found to be about four parts salt to five parts feldspar. By increasing the mass of salt from this to about six parts to about five parts feldspar a fair extraction was obtained. The foregoing experiments disclosed the facts, that the extraction was proportional to the amount of salt added and also to the temperature at which the mixure was heated. The next step was a series of tests made by heating in an assay muffle so that the temperature be more uniformly controlled. The following are the results obtained. (See Table III.)

The law of mass action evidently enters into this reaction also, and by increasing the mass of salt a complete extraction could be obtained, but by so doing would again make the process worthless from a commercial standpoint by decreasing the per cent of potassium in the final product. For example, take the best extraction obtained, 84 per cent, or 7.60 per cent of the potash. This would give only 5.06 per cent potash in the final product, which is as low as could be worked profitably. There is one great advantage in this process which may make it valuable. It could be used in connection with the manufacture of hydrochloric acid. The feldspar could be added to the salt and sulphuric acid and a by-product containing soluble potash would be left in the residue, with no loss of hydrochloric acid.

TABLE I.—GYPSUM METHOD.

No.	—Proportion— Parts of Feldspar.	Parts of Gypsum.	No. of Fullpower Bunsen Flames.	Time of Heating.	Per Cent K_2O Extracted.	Per Cent Extraction.
1	2	1	1	2 hrs.	1.36	15.00
2	1	1	1	1 hr.	1.72	19.00
3	1	2	2	1 hr.	2.47	27.40
4	1	8	2	2 hrs.	8.84	98.00

CALCIUM FLUORIDE METHOD.

Since hydrofluoric acid is the best solvent for silica it was reasoned that it might be used to dissolve this constituent and leave the potassium and aluminum free to unite with a mineral acid. Calcium fluoride (CaF_2) being the most available compound of fluorine it was used with sulphuric acid to form the hydrofluoric acid, according to the following reaction: $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$, or with feldspar $K_2O\ Al_2O_3\ 6SiO_2 + CaF_2 + H_2SO_4 = 12CaSO_4 + 6SiF_4 + Al_2O_3 + K_2O + 12H_2O$. The amount of calcium fluoride necessary to complete the reaction is 0.84 grams to 0.5 grams feldspar. Only one test was run using these proportions and only 37 per cent extraction was obtained. It is out of the question to increase the mass here.

TABLE II.—SALT AND SULPHURIC ACID METHOD.

No.	—Charge— Feldspar Grams.	NaCl Grams.	H_2SO_4.	Time of Heating.	Method of Heating.	Per cent K_2O.	Per cent Extraction.
1	.5	.12	Excess	1 hr.	Hot Plate	1.25	13.85
2	.5	.15	Excess	20 mi.	Dull Redness	0.32	3.55
3	.5	.15	Excess	30 mi.	1 Flame	0.78	0.86
4	.5	.15	Excess	45 mi.	2 Flame	4.32	47.89
5	.5	.15	Excess	45 mi.	Dull Redness	1.66	18.40
6	.5	.25	Excess	40 mi.	1 Flame	3.12	34.59
7	.5	.25	Excess	1 hr.	2 Flame	3.79	42.01
8	.5	.25	Excess	1 hr.	Dull Redness	1.57	17.40
9	.5	.5	Excess	1 hr.	2 Flame	5.56	61.64
10*	.5	.25	Excess	20 mi.	Blast	2.96	32.81
11*	.5	.36	Excess	10 mi.	Blast	4.05	44.67
12*	.5	.36	Excess	10 mi.	Blast	4.36	48.34
13*	.5	.36	Excess	20 mi.	Blast	5.32	59.00
14†	.5	.36	Excess	20 mi.	Blast	5.76	63.85
15*	.5	.36	Excess	20 mi.	Blast	5.32	59.00
16†	.5	.31	Excess	15 mi.	Blast	4.87	54.00
17‡	.5	.6	Excess	20 mi.	Blast	7.60	84.62
18§	.5	.41	Excess	20 mi.	Blast	5.08	56.32
19‡	.5	.41	Excess	20 mi.	Blast	4.50	49.88

*Heated for 1 hour before blasting. †Heated for 45 minutes before blasting. ‡Heated for 1¾ hours before blasting. §Heated for 1 hour and 10 minutes before blasting.

PHOSPHATE ROCK METHOD.

One more method was tried to a very limited extent. From previous experiments (gypsum method) it will be noted that dicalcium silicate was formed. If the calcium from the ordinary phosphate rock could be used to unite with the silicate of feldspar, we would then have a final product containing both potash and phosphorus, which would make it doubly valuable as a fertilizer. With this in view the amount of phosphate rock necessary to unite with the silica of the feldspar was figured to be about 1.12 grams when 0.5 grams of feldspar was taken. Sulphuric acid being also added in slight excess. This mixture was heated as in previous experiments and extracted with dilute sulphuric acid. Two tests were made by this method, both giving low results, one 21 per cent and the other 22 per cent extraction.

TABLE III.—SALT AND SULPHURIC ACID METHOD HEATED IN ASSAY MUFFLE.

	Charges						
No.	Grams Rock.	Grams NaCl.	H_2SO_4.	Time of Heating.	Approximate Temperature, Degrees C.	Per cent K_2O.	Per cent Extraction.
1*	.5	.31	4 drops	1 hr.	1,000	4.25	47.12
2*	.5	.4	4 drops	1 hr.	1,000	5.08	56.32
3*	.5	.5	4 drops	1 hr.	1,000	4.36	51.36
4†	.5	.31	4 drops	2 hrs.	1,200	5.14	57.00
5‡	.5	.4	4 drops	2 hrs.	1,200	6.63	73.50
6‡	.5	.5	4 drops	2 hrs.	1,200	7.42	82.26

*Did not fuse. †Black glassy fusion. ‡Green glassy fusion.

The foregoing experiments cover well the investigation of the principles of many of the old methods as well as the new ones here worked out, and while ideal results were not obtained, many new and interesting facts were brought to light. All work was done with extreme care and developments watched very closely. No results are tabulated here that were at all doubtful.

The above paper is a thesis presented by Mr. Quinney to the faculty of the State School of Mines for the degree of Metallurgical Engineer. It is of interest to note that subsequent to the presentation of the thesis Mr. Quinney and Professor M. F. Coolbaugh did a considerable amount of investigation with the idea of developing if possible a process for the production of potassium and aluminum in a commercial way. This subsequent work resulted satisfactorily and in connection with Attorneys C. L. Lewis and J. F. Schrader of Rapid City they secured a patent. A brief description of this patent is given in the *Official Gazette* of the United States Patent Office, Vol. 210, No. 2, Tuesday, January 12, 1915. The patent is No. 1,125,007 and is entitled *Process of Producing Soluble Salts of Potassium and Aluminum.* A description is given in the above named publication as follows:

1. The herein described process of producing soluble salts of aluminum and potassium from siliceous rocks, earths or minerals, containing insoluble compounds of potassium and aluminum, which consists in reducing the rocks, earths or minerals to a powdered form, mixing therewith limestone, heating the mixture to incipient fusion, cooling quickly, leaching the product with dilute sulfuric acid in the approximate proportions of one and two-tenths sulfuric acid by weight to each one part of potash by weight and three parts of sulfuric acid by weight to each one part of alumina by weight, and subsequently separating the potassium and aluminum sulfates from the resulting solutions.

2. The herein described process of producing soluble salts of aluminum and potassium from siliceous rocks, earths or minerals containing insoluble compounds of potassium and aluminum, which consists in reducing the rocks, earths or minerals to powdered form, mixing therewith limestone in the approximate proportions of one and seven-tenths parts of limestone, by weight, to each one part of silica, by weight contained in said rocks, earths, or minerals, heating the mixture to incipient fusion, cooling quickly, leaching the product with dilute sulfuric acid, and separating the potassium and aluminum sulfates from the resulting solutions, by crystallization.

3. The herein described process of producing soluble salts of aluminum and potassium from siliceous rocks, earths or minerals containing insoluble compounds of potassium and aluminum, which consists in reducing the rocks, earths or minerals to a powdered form, mixing therewith limestone in the approximate proportions of one and seven-tenths parts of limestone by weight to each one part of silica by weight contained in said rocks, earths, or minerals, heating the mixture to incipient fusion, cooling quickly, leaching the product with dilute sulfuric acid in the approximate proportions of one and two-tenths parts of sulfuric acid by weight to each one part of potash by weight and three parts of sulfuric acid by weight to each one part of aluminum by weight, and subsequently separating the potassium and aluminum sulfates from the resulting solutions by crystallization.

REGULATION OF ELECTROTYPING SOLUTIONS.

A preliminary study of the problems of electrotyping is now being conducted by the Bureau of Standards, Department of Commerce, in co-operation with a special committee of the International Association of Electrotypers. From the results of this preliminary work it is hoped to outline and conduct a more exhaustive investigation of these problems.

A circular has been prepared by the Bureau of Standards to meet the demands of electrotypers for such information as is available on the operations involved in copper and nickel electrotyping. Owing to the small amount of exact scientific information known to exist upon the subject, the present edition of the circular is confined to a general discussion of the possible results of such work and to simple methods for testing and adjusting the acid copper sulphate electrotyping baths. This circular, which is known as Circular No. 52 of the Bureau of Standards, entitled "Regulation of Electrotyping Solutions," may be obtained free of charge to interested parties upon application to that bureau, Washington, D. C.

MINERAL PRODUCTION OF THE WORLD.*

Table shows, in kilos of 2.2046 pounds for gold and silver and in metric tons of 2,204.6 pounds for other metals, the world's output of certain minerals and metals in 1912:

TABLE I.

Countries.	Coal. Tons.	Copper. Tons.	Fine gold. Kilos.	Iron. Tons.	Lead. Tons.	Fine silver. Kilos.	Tin. Tons.	Zinc. Tons.
Australia	11,918,018	41,000	72,344	33,201	217,120	492,450	6,745	199,926
Austria-Hungary	51,668,854	1,300	3,136	1,986,460	19,600	63,724	24	7,420
Belgium	22,972,140	....	....	60,000	70	....	......	400
Bolivia	....	3,765	78	....	....	123,939	23,168	1,863
British India	14,942,340	209	16,634	383,000	8,340	2,907	287	....
Canada	13,165,826	35,305	19,032	72,826	16,222	993,942	......	3,100
Chile	1,334,407	41,647	1,101	4,387	5	39,468	......	....
China	13,190,000	392	5,505	23,997	680	....	8,783	1,816
Dutch East Indies	577,448	....	3,931	....	....	13,941	20,232	....
France	41,145,178	33	3,505	7,700,000	9,980	18,460	......	14,620
Germany	255,810,100	27,410	118	8,474,360	77,786	190,000	......	240,596
Italy	663,812	2,748	38	306,109	24,453	14.363	52	56,496
Japan[2]	20,028,211	63,892	13,644	94,501	3,733	153,728	198	7,487
Mexico	2,450,000	73,000	36,864	1	109,720	2,321,626	......	15,550
Netherlands	1,725,397	....	....	....	....	....	......	....
New Zealand	2,212,560	....	9,672	....	....	24,919	......	....
Peru	278,927	26,970	1,435	....	4,050	324,352	......	....
Russia	31,296,900	33,550	43,562	4,198,000	1,000	6,224	......	11,100
South Africa	7,363,693	7,741	283,315	....	570	31,695	1,773	....
Spain	4,136,309	60,610	....	4,447,510	170,100	160,268	131	60,810
Sweden	360,291	425	31	4,168,000	2,512	1,002	......	21,984
United States	484,864,901	563,943	140,608	30,665,595	376,844	1,983,371	123	293,847
United Kingdom	264,595,395	296	41	4,523,074	19,461	3,825	5,338	6,159
All other	3,195,278	44,247	57,889	5,270,460	72,998	219,314	58,864	74,575
Total	1,249,895,985	1,031,483	712,483	72,411,481	1,135,244	7,183,518	125,718	1,017,749

[1] Certain provinces only. [2] Including Taiwan and Chosen.

The principal items included in "all other" are as follows: Norway—15,240 tons of copper, 198,800 tons of iron, and 8,406 kilos of silver; Roumania—242,025 tons of coal (1911); Gold Coast—10,997 kilos of gold; Rhodesia—20,033 kilos of gold and 6,886 kilos of silver; Newfoundland—661,471 tons of iron; Cuba—857,756 tons of iron; Algeria—654,500 tons of iron, 9,783 tons of lead, 4,560 kilos of silver, and 37,033 tons of zinc; Tunis—239,200 tons of iron, 24,700 tons of lead, and 16,400 tons of zinc; Greece—220,825 tons of iron, 15,368 tons of lead, 21,979 kilos of silver, and 8,700 tons of zinc; Luxemburg—2,344,030 tons of iron; German Southwest Africa—11,257 tons of lead and 11,663 kilos of silver; Turkey—745,676 tons of coal, 11,000 tons of lead, and 46,940 kilos of silver; Columbia—18,279 kilos of silver; Costa Rica—18,004 kilos of silver; Honduras—65,591 kilos of silver; Federated Malay States—47,988 tons of tin; Siam—6,669 tons of tin; Indo-China—430,260 tons of coal and 10,279 tons of zinc.

The total production of petroleum was 47,186,463 tons, and of salt, 17,970,253 tons. The United States led in the production of petroleum with 29,620,201 tons, and was followed by Russia with 9,317,700 tons; Mexico, 1,992,290 tons; Roumania, 1,835,940 tons; Dutch East Indies, 1,518,348 tons; Austria-Hungary, 1,146,926 tons; and British India, 1,000,341 tons. The largest quantity of salt also (4,232,489 tons) came from the United States, while the United Kingdom produced 2,156,307 tons; Russia, 2,054,301 tons (1910); Germany, 1,967,924 tons; British India, 1,311,958 tons; France, 1,098,525 tons; Austria-Hungary, 797,940 tons; Japan (including Taiwan and Chosen), 777,064 tons; and Italy, 524,349 tons.

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*British Mines and Quarries Report, Part IV.

GRAPHITE AND STRENGTH OF CASTINGS.*

The deleterious effects of graphite were emphasized by Dr. J. E. Stead in a recent lecture in Birmingham, England, on "Some Scientific Features of Cast Iron." He described graphite as the enemy of the foundryman and likened it to thin plates of mica which can be split along their cleavage planes with the utmost ease. He summarized the results of a large number of tests, undertaken with a view of ascertaining the influence of graphite on the strength of castings, in the following table:

Graphite, per cent.	Transverse Strength, cwt.	Tenacity, Tons.
3.00 to 3.25	20.4	8.25
2.60 to 2.85	27.1	13.24
2.15 to 2.55	31.9	14.54
2.00	40.0 above	17.10
None, with 3 per cent silicon	91.0	88.60

He deprecated the rule-of-thum practice which has led foundrymen to adopt a hostile attitude towards types or grades of pig iron with which they were unfamiliar, citing the case of some irons of superlative quality which were unsalable and had to be reinserted because their fracture presented some unusual features. He argued that any class of iron could be made to yield the results desired if only it were "mixed with brains"; that even sulphur, sometimes considered the foundryman's worst enemy, could be turned to useful account if intelligently handled. This element should rather be regarded as a friend, said Dr. Stead, because it prevents the carbide from parting with its graphite.

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*From The Iron Age.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

Funds for the United States Geological Survey.

The sundry civil act as passed by the last session of Congress contained appropriations of $1,355,520 for the United States Geological Survey. Most of the appropriations for the Survey are included in this great Government supply bill, but in addition to the above-stated amount $40,000 was appropriated in the legislative bill for rents, so that the total amount appropriated is $1,395,520. The principal items in the appropriations for the Geological Survey for the fiscal year ending June 30, 1916, are as follows:

Topographic surveys	$350,000
Geologic surveys	350,000
Mineral resources of Alaska	100,000
Mineral resources of the United States	75,000
Chemical and physical researches	40,000
Geologic maps of the United States	110,000
Gaging streams, etc	150,000
Surveying national forests	75,000

The bill also appropriates $175,000 for printing and binding Survey reports, to be expended by the Public Printer, and $1,500,000 for the new Interior Department building, which is to accommodate the Office of the Secretary of the Interior, the Geological Survey, the Reclamation Service, the Land Office, the Indian Office, and the Bureau of Mines, all bureaus of the Interior Department whose work is closely related to that of the Survey and among all of which there is more or less constant co-operation. The total cost of the new building has been fixed at $2,596,000.

Sulphuric Acid in Germany.

The effects of the war on the German sulphuric acid industry are dealt with by Herr K. Reusch in the Chemiker Zeitung. The following abstract of the article is given by the English paper *Fertilizers*. The export of sulphuric acid, sulphuric anhydride, and sulphurous acid from Germany is now prohibited. The total German production of sulphuric acid in 1912 was 1,649,681 metric tons, calculated as monohydrate; and in 1913 the imports exceeded the exports by 65,289 metric tons, most of the imports being from Belgium. Of the requisite pyrites, more than 80 per cent was imported, mainly from Portugal, Spain and France. The working of the considerable German deposits might present difficulty owing to scarcity of labor. Norway is indicated as a further possible source of supply. No data are available respecting the amounts of nitre and nitric acid used in the manufacture of sulphuric acid; but in 1911 the contact process was employed in seven of the works, the chamber process in eighty-six, and both processes in seventeen. The price of nitre has risen; and discussing sources of such material, reference is made to the Norwegian production and the present strenuous German efforts to convert ammonia into nitric acid on a large scale. In view of the increased demand for sulphuric acid in manufacturing explosives, the price has risen slightly, and it is recommended that some economy should be made in the superphosphate industry, for which 600,000 metric tons of acid were used in 1913.

Demand in Japan for Imported Paints.

According to an extract from *Japan Advertiser* of Feb. 9, by Consul General George H. Scidmore, Yokohama, the supply of imported paints from the European Continent has practically been stopped since the war opened, what little now is imported being from England and the United States. Under the circumstances the stock is gradually decreasing in the home market, while the foreign supply, which was about 8,267 pounds per month in average prior to the war, is at present scarcely half that amount. The quotations for the imported goods are now about 10 per cent higher than those ruling before the war, and those for homemade paints are nearing the prices of foreign goods. At present the differences in prices between the imported and the homemade paints is about 10 per cent, the latter being, of course, cheaper; but the shortage of the foreign stock has caused the larger demand for homemade goods, except for particular purposes where imported paints are preferred. The imported paints of English production are now being quoted at $13.70 per 112 pounds, while the homemade paints are quoted at $12.45 per 112 pounds. As to the supply of lead and zinc which is to be used as material for paints, a greater portion of these metals produced in Europe is said to be used for the purposes of war, and the supply from Belgium, on which the Japanese paint factories have relied, has now entirely been stopped. Therefore, it is expected that the market for these metals would tend to be tightened. As to the future prospect of the demand for paints it is generally believed that a large demand would be felt in April on account of the Government purchase due at the beginning of a new fiscal year, and also on account of the advent of the usual brisk season for paints. Another reason for the future briskness is that the shipping business has recently improved to a large extent, and after a few months a big demand for ship's paints is expected. As to the present quotation for ship's bottom paints, the superior stuff, No. 1, is valued at $30.88 per 112 pounds and No. 2 at $28.68 per 112 pounds.

Sound Steel Ingots and Rails.

The United States Bureau of Standards is engaged in an experimental investigation of the causes of failure of railway materials. A matter of fundamental importance is the effect of the ingot upon the character of the rails produced. The several methods of producing sound ingots are being studied with the cooperation of the makers. An examination of one improved type of ingot has been made and very satisfactory results obtained. Rails from several ingots of this type were rolled at the Maryland Steel Works. Preliminary results were presented before the American Institute of Mining Engineers at the annual meeting in February, 1915, under the title "Sound Steel Ingots and Rails." A more complete account will be published later as a technologic paper of the Bureau of Standards.

Dyestuff Situation in England.

The progress of the movement in England to manufacture at home the supply of dyestuffs formerly imported from Germany has been noted from time to time in Commerce Reports (Nov. 3, Dec. 14 and 28, 1914, and Jan. 7, Feb. 18, and March 18, 1915). In addition to the matter published, there has been received from Consul W. Henry Robertson, of Manchester, a number of newspaper clippings, comprising editorials and letters from interested scientists and manufacturers, which together make an interesting history of the whole movement. The last clipping received is the prospectus of the new Government-backed company, "British Dyes, Limited," as printed in the Manchester Guardian. The collection of clippings will be loaned to interested persons by the Bureau of Foreign and Domestic Commerce, Washington.

GERMAN POTASH SITUATION.

U. S. Consul-General Julius G. Lay, Berlin, in a report dated March 10 states that although exports of potash were forbidden by the German Government Jan. 29, 1915, the executive authorities of the German Potash Syndicate have resolved to authorize the following deliveries for domestic and foreign consumption during 1915, so that in case the embargo is removed the potash interests will know the amount that can be shipped and be in a position to make immediate delivery in accordance with the potash law of 1910 (the value of these potash salts as fertilizers depends upon the percentage of pure potash, K_2O, contained in them, and the quantities given in this table are net tons of K_2O, not gross tons of the salts):

	Metric tons of pure potash, K_2O.	
Kinds of potash.	Domestic.	Foreign.
Carnallite with at least 9 and less than 12 per cent K_2O	4,800	300
Raw salts with 12 to 15 per cent K_2O	266,600	82,200
Fertilizer salts with 20 to 22 per cent K_2O	2,000	33,400
Fertilizer salts with 30 to 32 per cent K_2O	3,600	11,500
Fertilizer salts with 40 to 42 per cent K_2O, including potash fertilizer with 38 per cent K_2O	229,200	68,700
Potassium chloride	54,500	138,300
Potassium sulphate with more than 42 per cent K_2O	1,200	37,600
Potassium-magnesium sulphate	200	14,700
Total	562,100	386,700

It will be noticed that the amount of potash that can be delivered for domestic and foreign consumption is 948,800 metric tons for 1915, as compared with 1,166,600 metric tons for 1914. The potash syndicate has conferred with the Imperial Government with a view to ascertaining some feasible scheme for denaturing potash salts so that the embargo can be removed and exportation again commenced to neutral countries. So far these plans have not materialized and the embargo still remains in force.

When the potash syndicate became convinced a few weeks ago that the embargo would not be removed it petitioned the Government to raise the selling price for domestic deliveries, which was fixed in the potash law of May 25, 1910. The causes that led to this petition were the cutting off of foreign exportation, the high cost of labor, and the decreased production. If the present scarcity of Chile saltpeter, Florida rock phosphates, and other foreign fertilizers continue, the domestic demand for agricultural purposes is expected to increase, although this increase will be comparatively small and will not compensate the producers for the discontinuance of the foreign shipments that are so significant in the German potash trade in normal times.

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THE CYANIDE PROCESS.*

By FRANK S. WASHBURN.

The fixation of atmospheric nitrogen has had commercial application for the past ten years. During this period different types of processes have been conceived; four, the Serpek, Haber, Arc and Cyanamid, have seriously attempted commercial exploitation; two, the "Arc" and "Cyanamid" processes, have proved to be commercially practicable in the broad sense. Of these two the latter may justly claim to be of great economic importance to the world because the unit of fixed nitrogen in its first product is capable of being more cheaply produced than by any other present-known process, and because this first product has a direct and valuable use of itself and constitutes the raw material for a varied and important line of derivatives into which, for the most part, it can be cheaply transformed.

The annual productive capacity of the existing plants employing the "Arc" and "Cyanamid" processes is between 90,000 and 100,000 net tons of fixed nitrogen, which, at the normal average value of the product at the factory door, represents $25,000,000. This is divided in the ratio of two-thirds to "Cyanamid" and one-third to the "Arc" process. The American Cyanamid Company's factory at Niagara Falls, Canada, has alone a capacity in fixed nitrogen approximately half as great as the total world's installed capacity by the "Arc" processes.

More than three thousand technical articles dealing with almost every conceivable phase of nitrogen fixation have appeared in different languages. The patents applying to the subject in all its branches number into the thousands. So far as the author of this paper knows, nothing has appeared in the nature of a differentiation of processes based on the economics of the world demand for nitrogen. It is only for a limited developmental period that the theoretical, technical advantages and limitations of related processes constitute a practical basis for hazarding opinions as to their ultimate commercial value. It is also true that until an art has had some years of commercial application it is impossible to analyze and draw sound conclusions from the economics of the situation, the final arbiter in determining the social value of any process.

The art of atmospheric nitrogen fixation is now old enough to enable one to see the economic aspects of the case, and therefore, in casting about to determine what part of this vast subject to deal with in this paper, the author thought it would be of interest and possibly of value to treat herein the broad commercial outlook for the various fixation processes, and in order to limit the matter to conditions more or less well known to all of us, conditions on the North American continent, for the most part, will be the only ones considered.

Two nitrogenous compounds, nitrate of soda and sulphate of ammonia, constitute in value 80 to 85 percent of the total raw nitrogen compounds produced throughout the world. The value of their combined production in 1913 was between $190,000,000 and $200,000,000. It is estimated that 80 percent went to agriculture, corresponding to an annual per capita tax on the 600,000,000 inhabitants of the earth of thirty-three cents.

Nitrogen has four main uses: as an agricultural fertilizer, as nitric acid and derivatives therefrom, as ammonia, and in dyes and various other chemical compounds. Measured in the quantity of contained nitrogen, and in view of the restricted opportunities in the United States for immediately developing the chemical and dye industries on a large scale, we need consider as bearing decisively on atmospheric nitrogen fixation processes only the three first-mentioned uses, namely, for crop fertilizer, for nitric acid and its derivatives, and for ammonia as such.

The farmers' purchases in nitrogen used east of the Mississippi River last year approximated $75,000,000. More than 90 percent of fertilizer nitrogen is in the form of ammonia. The normal annual consumption of nitric acid in the same region is about $7,000,000. The price paid per unit of nitrogen is about the same for each, and the percentage annual increment of consumption is about 10 percent in each case. However, the importance of the fertilizer field in comparison with the nitric acid field, in their bearing on the fixation of atmospheric nitrogen, is not fully nor even approximately measured by this ratio of ten to one.

The use of nitric acid is along established lines looking comfortably to the future for a steady growth, with no serious limitations hampering modest development and no great unsatisfied human need demanding great development. It is essentially a small business as great industries go. The fertilizer industry has a very different significance. The population of the United States from 1900 to 1910 grew from 76,000,000 to 92,000,000, an increase of 21 percent. Crop production increased 10 percent in the same period. Exports of wheat and flour decreased from 31 percent of their production to 13 percent. The importation of foodstuffs and live animals practically doubled, while imported manufactured foodstuffs more than doubled. Beef cattle production fell off 32 percent as the population increased 21 percent. These figures are strikingly reflected in the increased cost of foodstuffs, which from 1896 to 1912 amounted to 80 percent in the United States, while the general advancement in the cost of living during this period was 59 percent in the United States, 40 percent in England, and 40 to 45 percent in continental Europe.

These facts point to the necessity of increasing crop yields without additional labor—and that defines fertilizer. European yields per acre cultivated are 50 to 100 percent greater than American yields. The use of fertilizer in Europe, per acre cultivated, is enormously greater than in America. The average increase in yield in Germany for the past twenty years has been approximately 60 percent, in the United States 20 percent. Abroad this increase is attributed to intensive farming, better selection of seed, the rotation of crops and, to the extent of 50 to 70 percent of the increase, to the use of commercial fertilizers.

The farmers' purchases of fertilizer in the United States last year in nitrogen and phosphorous constituents (later it will be shown why both are here included) was approximately $150,000,000. Were the cultivated lands east of the Mississippi to receive for each of two years out of every three the quantity of fertilizer normally used per acre each year in Germany, the bill would have been approximately $1,600,000,000, or ten times as great as the actual expenditure. The very limited use of fertilizers in the United States does not arise from the possibility that fertilizers do not pay. Indiana experiments, conducted in ten counties, produced an average increase of 11.6 bushels of wheat per acre, valued at $11.60, for an expenditure of $3.67. An instance of a very low return in the use of fertilizers is an unpublished record of thirty-seven experiments in Illinois in 1913, showing an average increase of 5.2 bushels of wheat, valued at double what the fertilizer cost.

The fertilizer industry today suffers many handicaps. These originate in part from the farmer's limited capital for properly conducting his business, his lack of knowledge which closes to him what would otherwise be avenues of advancement and prosperity, and in part also from the fact that there is no vital, broadcast propaganda and educational bureau conducted by the fertilizer industry itself.

The greatest handicap is possibly in the material used. The industry is carried on by collecting at a great number of places throughout the agricultural regions east of the Mississippi a great variety of materials, each containing some one of the so-called plant foods, namely, nitrogen, phosphorus and potash, the last representing only about 10 percent of the total. For the most part these materials are low in fertilizing value, and when mixed in a manner to include the low as well as the high-priced materials, there results of necessity a product of which 85 to 90 percent is useless dead weight, only the small remainder having fertilizer value. Forty percent of the annual fertilizer product in value is in the nitrogen constituent drawn from materials that are either by-products or wastes, such as sulphate of ammonia, slaughter-house refuse, fish scrap, vegetable refuse, waste of sugar works and distilleries, hair, leather, wool, hoofs and horns. The phosphoric acid constituent is secured from acid phosphate analyzing from 14 to 16 percent P_2O_5, and as a general rule constituting one-half of the complete fertilizer mixture. Few of these raw materials in the broad sense are satisfactory. They are borne with because up to the present time there are no others commercially available. They pay the uttermost limit in the way of transportation charges to the point of their preparation, and after being mixed they bear a further great transportation burden to the consumer's railway station. There is a relatively large expense for mixing, storing, drying, bagging and selling. After the farmer has received his goods at the railway station, he must haul over spring roads, often almost impassable, 1,000 pounds of material in order to get 150 pounds of plant food. It is one of the recognized, recurring, contributing causes for small crops, particularly in the South, that the roads are so bad in the spring, due to rains, that farmers cannot haul the necessary amount of fertilizer.

Notwithstanding the consumer pays for nondescript materials, requiring only to be mixed in the crudest manner, a price 60 per cent greater than their spot value, the fertilizer industry as a whole, which prepares and sells the product, is conducted without measurable profit.

Unless revolutionary developments in some vital respect come to the aid of this great industry in the United States, any marked improvement is impracticable. It would appear, for reasons already set forth, that possibly the matter of greatest economic importance in the United States today is that conditions shall be brought about by which the farmer will use a vastly greater quantity of fertilizer than is now used. We believe the most important single contribution to this end would be a high-grade chemical salt containing nitrogen and phosphorus, well balanced and in large percentages, and possessing in a high degree the many requisites of a good fertilizer, such as being non-hygroscopic, non-toxic, finely granular in form, non-leachable in the soil and readily convertible by nature's forces into the organism of the plant. The process for the fixation of atmospheric nitrogen that will contribute the nitrogen content to such a fertilizer compound to the greatest net advantage may be justly viewed as the most important, not only to society, but also therefore to those who exploit it.

Discussions of the ultimate commercial superiority of a favorite process and the consequent complete annihilation of every other have been almost interminable. These have proceeded apart from any broad conception of time, place, the demands of mankind or the quantitative application of the product. They generally take the form of rival claims for cheapness in the cost of production, and this without much reference as to whether the unit cost applied to a form of nitrogen for which there was any particular or large demand, and without reference to whether the product was to be produced at a place and in a form enabling is to be transported to the consumer.

The Serpek process was discussed by volunteer adherents without knowledge that per unit of nitrogen fixed the necessary expenditure of heat energy from electricity alone is as great as the total electric energy consumption in cyanamid. Therefore, no suspicion was aroused that possibly nature had not placed the necessary raw material, bauxite, within practically shipping distance of equally necessary cheap water powers. The limitations of the by-product, upon which the commercial possibilities of the process depend, were not questioned either as to the difficulties in converting it to commercial aluminum or as to the relation of its volume to the market demand for the metal.

The Haber process has been taken by the public for granted as one practicable of universal application because of its larger though single use by a great concern of brilliant accomplishments in the commercial chemical world. The public does not know of the pressing problem of disposing of great quantities of sulphuric acid, and the single problem involved of how, under the local conditions, to devise the cheapest possible means of providing the requisite ammonia for using the acid in sulphate of ammonia. The electric energy necessary to the process is generally considered negligible, and yet a proposal to establish a plant close to New York involved, at the necessary power cost in that vicinity, as great an expense for electric power as the total power cost for cyanamid in an available site then under consideration for that process.

Air nitrogen fixation processes divide themselves into two broad classes, namely, those that come in at the nitric acid end, and those that come in at the other extreme, the ammonia end. There is no expectation that the various "arc" processes producing nitric acid will ever have employment in the production of ammonia compounds, for the sufficient reason that there is no prospect of ever being able to commercially convert nitric acid to ammonia. Therefore, the best that can be said of the "arc" processes is that they may be able, by reason of having nitric acid as their first product, to occupy exclusively the field for the production of nitric acid. We have already seen that this field is not only relatively but absolutely a limited one for the present, as it is prospectively for the future.

The "ammonia" processes are not ready to admit, however, that there is an insurmountable barrier separating them from the nitric acid field. A tried, thoroughly workable, commercial plant for the oxidation of ammonia into nitric acid is not yet complete and in entirely satisfactory operation, but, on the other hand, the various steps necessary to the operation of such a plant have been separately brought to such stages of development as to leave no doubt in the minds of the experienced men who have worked upon the problem of the ultimate complete commercial practicability of carrying the ammonia processes for the fixation of atmospheric nitrogen through to the nitric acid producing stage.

A powerful factor operating as a disadvantage in the "arc" processes to the manufacture of nitric acid is the extraordinary difficulty of transporting the acid from the remote, cheaply developed water powers, very limited in number, where alone these processes can be employed, to the place of use for the acid, both sea and rail transportation being practically invariably necessary. This audience does not need to be told how serious a matter is this. The nitrate compounds made from acid produced by the "arc" processes have found no place as a fertilizer in this country. Nitrate of lime, even in the so-called basic form, is too strongly hygroscopic to permit its use alone or as part of a mixture to be used through the ordinary drills by which fertilizer is distributed to the soil in this country. Even if the physical form were entirely satisfactory, it could not satisfactorily have a very large place in fertilizer mixtures in this country because of its being too readily available in the soil and because the valuable form of fertilizer nitrogen is as ammonia and not as nitrate. We have seen furthermore that the fertilizer industry demands something more than a new nitrogenous material, however meritorious it may be, merely as an additional one to the many which now constitute a part of a complete fertilizer mixture.

For a time it was thought that the treatment of phosphate rock by nitric acid might possibly find a large place in the fertilizer world. Two decisively unfavorable and irremedial results have developed from this attempt; first, the product is excessively hygroscopic, the surface when exposed taking up sufficient moisture to reduce the external parts to a molasses-like condition, and second, the content in plant food, approximately 11 percent nitrogen and 14 percent phosphoric acid, is markedly lower than that readily securable in the new commercial ammonium phosphate compounds resulting from the combining of ammonia and phosphoric acid. When carried to the monocalcic stage, thereby giving it the desired water solubility, the excess acid is of necessity so great that the crop is burned and destroyed. Much money has been spent on these efforts, which have always resulted in failure.

This brings us now to the consideration of the practicability of an ammonia-phosphoric acid compound for agricultural use. The mono-ammonium phosphate, containing theoretically 14.6 percent of ammonia and 61.3 percent of phosphoric acid (P_2O_5) and the di-ammonium phosphate, containing theoretically 21.8 percent of ammonia and 53.4 percent of phosphoric acid, have been recognized by the scientific world for many years as fertilizers of extraordinary value, being in effect perfect materials, as they possess every qualification of a good fertilizer. The manufactured product made in this country has not developed any limitation. Under some circumstances, at least, the results in crop increase are greater per unit of ammonia and phosphoric acid than is securable from any other fertilizer or fertilizer compound, and the question has arisen whether this salt may not produce its result partially from the exercise of the same natural laws that apply to the action of manganese sulphate, for instance, in which there is a crop increase that cannot be attributed to the taking up by the plant of anything contained in the fertilizer. The effect may some day be safely attributed to the inducement that the salt has given to increased activity of the chlorophyl and thereby increased power of assimilation on the part of the plant.

The commercial ammonium phosphate product may be readily produced at will with varying proportions of ammonia and phosphoric acid, ranging from 13 and 47 to 21 and 46 percent respectively. Thus it is that the plant food constituents of this single material, varying between 60 and 67 percent, occupy the entire range of the usually desired relationship between ammonia and phosphoric acid. The phosphoric acid content of the commercial acid phosphate now used in agriculture, a product which, roughly speaking, results from pouring a ton of 52° sulphuric acid on a ton of rock containing 30 to 32 percent P_2O_5, contains about 14 to 16 percent P_2O_5. In value it constitutes about one-half the farmer's fertilizer bill in the United States each year. Whatever advantages a new kind of phosphoric-acid-containing material may have, it should be capable of being produced at a cost no greater than the percent unit cost of phosphoric acid in acid phosphate.

Two methods of manufacturing ammonium phosphate compounds have been developed. One of these is in the proved commercial stage and can produce as cheaply, at least, as by acid phosphate. The other is in the advanced developmental stage and promises still cheaper production costs. The first is applicable wherever cheap sulphuric acid may be had, and the second, which employs the electric furnace in driving off phosphorus from the phosphate rock, is applicable only where there is cheap water power available.

When the problem is referred to the actual conditions existing on the North American continent, the most available process known for providing agriculture in a broad way with the ammonia constituent of an ammonium phosphate compound is the "cyanamid" process. Searching investigation and analysis, for four years, of prospective cyanamid manufacturing sites, covering the United States and Canada, has developed a state of facts establishing the practicability of placing ammonia at the disposal of agriculture and the arts in practically every place of large use in the United States, and cheaper and simpler than could be accomplished in any other way. This may be done by shipment of cyanamid from a central point of manufacture to these various localities and its conversion there into ammonia.

These natural tendencies towards the "Cyanamid" process as the principal source for nitrogen supply might be turned aside, however, unless that material and its important derivatives, notably ammonia, could be produced and delivered to the consumer cheaper than by other means and through the employment of capital in such a manner as would induce the investment of money in the undertaking. This brings us then to a consideration of the costs of production applied to a distinctive set of conditions which correspond not only with all the important conditions surrounding the demand for and use of the product but also those which characterize an actual place of production and its geographical relation to the consumer.

There is properly a hesitancy on the part of any business enterprise to disclose actual costs. Such information is frequently made wrong use of, and the risk involved in making it public is wholly out of proportion to the gain. At the same time the author realizes that without volunteering exact statements of comparative cost figures, open to confirmation or refutation, as the case may be, it is difficult to carry conviction to the hearer that one's conclusions are sound. The founders of the American Cyanamid Company have not from the beginning been wedded to any particularly process for the fixation of atmospheric nitrogen. The aim and policy has been to conduct the company's activities and research work toward the end of developing a great nitrogen industry. It has investigated many processes with the conviction that it could not hope to have permanent and ultimate success except through the application of the best. Its research work in entirely new fields, and in the regular manufacture of its product, has been practically continuous from the day it first began commercial operations in 1910. It is therefore natural that those connected with the company should feel confident of their judgment on many matters bearing upon the relative merits and limitations of various nitrogen fixation processes.

Therefore, while it may be impolitic to disclose actually attained minimum costs it may be possible to establish particular facts and comparisons which will by their logic carry conviction as to the order of compared processes so far as production costs are concerned, without, however, expressing the exact differences in costs. For instance, by the "arc" process the factory cost of nitrogen in commercial nitric acid, excluding all power costs (derived by applying actual working records to a particular manufacturing site where all conditions are of the most favorable nature) is greater than the total cost of nitrogen in "cyanamid" including power at $10 per continuous horsepower per annum (at a site where raw materials and labor are relatively high). Furthemore, taking that particular "arc" process which is the lowest in power consumption, the power cost alone, at eight to ten dollars per continuous horsepower per annum in weak nitric acid is greater than the total cost of "cyanamid," including power at the same cost per horsepower per annum (and at a site where raw materials and labor are high). These are actual comparisons and lead conclusively to some irrefutable deductions; first, that the "cyanamid" process can fix nitrogen cheaper than the cheapest of the "arc" processes, even although a charge of ten dollars per continuous horsepower per annum is made against "cyanamid" and the power is given free to the "arc" process; second, if the cheapest of the "arc" processes, so far as power consumption is concerned, is charged only with power at the rate of eight to ten dollars per continuous horsepower per annum and the process is presented without cost or charge of any sort with all labor, raw materials and supplies, its unit of nitrogen would cost more than the total cost of the unit of nitrogen by the "cyanamid" process. It also follows from these conditions that the total cost of the unit of nitrogen in commercial nitric acid made by the "arc" process cannot by any chance be less than double the total cost of the unit of nitrogen in cyanamid made by the "cyanamid" process. We have seen that the really great application of nitrogen is at the ammonia end and these comparisons are impressive in showing not only that there is no hope of the "arc" process working into ammonia production but also, and what is of more importance, that the "cyanamid" process has to its credit a wide margin of saving in cost to span the gulf between "cyanamid" and nitric acid.

The first step in the derivation of nitric acid from cyanamid is to convert the latter into dry ammonia gas. Such conversion is now conducted in so many places and on so large a scale that the actual cost of the operation, including all losses, is no longer a matter of speculation or approximation. The efficiency has been raised in actual practice to over ninety-nine percent and the cost, while not negligible, is so low as to add only a small percentage to the ordinary cost of the unit of nitrogen in "cyanamid." Therefore, the facts just set forth as to the cost of the unit of nitrogen in "arc" process nitric acid, compared with the cost of the unit of nitrogen in cyanamid, apply as well to the cost of the unit of nitrogen in pure ammonia gas. Roughly speaking, therefore, there is to the credit of the ammonia, available for oxidizing it to weak nitric acid, fully one-half the cost of weak nitric acid derived by the "arc" process. As a matter of fact, the indications are that this span will be bridged by the absorption of not more than one-half this difference, making weak nitric acid by the "cyanamid" process cost approximately three-quarters of the "arc" process. As power is brought below ten dollars per continuous horsepower per annum, production costs by the "arc" processes approach more nearly to costs by the "cyanamid" process. It is possible to make the general statement that the costs per unit of nitrogen in weak nitric acid may be taken as the same for both processes where power costs about $4 per continuous horsepower year.

Comparison of the costs of ammonia gas by the "cyannmid" process and the "Haber" process show, broadly speaking, that the Haber process in its most favorable environment involves a cost nearly double that of the "cyanamid" process under favorable conditions practicable of attainment.

It must not be understood that the "cyanamid" process has exhausted the possibilities of further economies in manufacture. As examples, in one new factory study in which the requisite coke is to be made by local by-product ovens, the operations so balance that the fuel gas derived is the quantity required, and as the tar and ammonia products pay for the coking, the coke is had at the price of coal. Where ammonia is derived at the cyanamid factory the sludge from the autoclaves composed of calcium carbonate and carbon may be turned back through the carbid furnaces and maintained in the cycle practically indefinitely as a carrier of nitrogen.

However, the whole story is not involved in a study of production costs, for there are other factors which may have a deciding voice, and of these we may mention as important the amount of the necessary investment for a given output, the salvage in the case of ultimate abandonment, the ratio of interest charge to the out-of-pocket expense, bearing in mind that the latter may be very much reduced by improved operating means while the former is fixed for all time. Taking the necessary investment in the "arc" process per unit of nitrogen in weak nitric acid as a basis, and assuming power to be placed upon the switchboard at an investment cost of $50 to $75 per horsepower, the corresponding investment in the "cyanamid" process for a unit of nitrogen in weak nitric acid would be about one-half, and as cyanamid or ammonia gas about one-third. It is believed that the Haber process in the United States on the same basis would involve an investment of about two-thirds to three-fourths of the "arc" process. In the contemplation of any enterprise requiring large fixed capital there is a reasonable amount of capital beyond which objections to an increased amount are not to be measured by applying the interest and amortization rate to the estimated costs of production. Converting a vast amount of gold in the bank into bricks and mortar, special machinery and appurtenances, particularly in the application of a new and special art is a serious risk for which there is no exact measure, but which in contemplating the risk should weigh heavily as a guide to judgment.

In the case of ammonia production by the "cyanamid" process the fixed investment may be as low as one and one-half times the annual value of the product and in the case of the Haber process three times. In the case of nitric acid by the "cyanamid" process the investment may be as low as one and one-fourth times the annual value of the product and in the case of the "arc" process with a power investment of $75 per continuous horsepower the fixed investment would be between three and four times the market value of the annual product.

The majority of manufacturing concerns in the United States vary in fixed investment from one to one and one-half times the value of the annual product and the inherent risk in industrial enterprises, for reasonably assured profits demand, for the most part, very special conditions where this proportion is exceeded. Even that class of investments considered most stable as to reliability, permanency and growth, namely, public utility corporations, do not exceed $4 to $6 investment per dollar gross revenue. We are therefore met in the case of the Haber and arc processes with the necessity for making an investment which, in the judgment and practice of the industrial world, is wholly out of proportion to the market value of the annual product, while in the case of cyanamid the requirements are within the limits of ordinary commercial practice.

These considerations serve to emphasize the difficulties in commercially advancing any new enterprise. The younger technical men do not encounter these difficulties and therefore do not give them due weight. There is extraordinary difficulty, particularly in the United States, in financing a new chemical enterprise, particularly if it involves a large preliminary expenditure in research and developmental work. The banker's attitude, and properly so, is to compare assets and liabilities. Buildings, equipment and manufacturing sites are acceptable assets notwithstanding that in many companies if the business itself were abandoned there would be little or no value in the physical properties. Knowledge, processes, and ideas are not impressive assets. They are considered in large part to have been something secured at great cost, but, even with good patent protection, practically available for the use of prospective competitors without cost to them. In some other countries such enterprises are viewed quite differently, notably in Germany, where ideas are the foundation of great and profitable enterprises and where by law and practice they are better protected for the exclusive use of those who have developed them than in this country.

The promise, or even the assurance of reasonable profit, is seldom a sufficient inducement to the investor to undertake a pioneer enterprise. The competitive element which dominates almost every other activity is lost sight of by the amateur promoter. He forgets that to the mind of the prospective investor he is in the sharpest kind of competition with those presenting other types and kinds of enterprises demanding capital. His project must grip the imagination with peculiar attractiveness as well as impress the practical sense of those to whom it is brought as not only being prospectively profitable but also assuredly safe with a minimum prospect of loss and a maximum prospect of profit. Of the many subordinate advantages there may be specifically mentioned an early dividend paying period, a ready market for the securities, their acceptance as good collateral, and a ground-floor prospect in future extensions. In the end it must outweigh, in some cases, literally scores of other projects all claiming equal if not superior merit in every particular. There is another consideration of kindred merit which will be impressive if one considers that in a thing so extensively engaged in as trade in securities, one of the very largest activities in which mankind interests itself, there must grow up inevitably certain more or less arbitrary rules, practices and points of view. These all turn naturally upon the usual thing, and the usual thing is the established industry, or at least an enterprise engaged in an established industry. Therefore, the new thing has a slow and difficult road to travel and its difficulties are more than in direct proportion to the amount of capital demanded. Those fixation processes which employ and own their own water powers make a plea to capital that others cannot make, for the reason that it can generally be shown that should unexpected competitive developments in the remote future drive the undertaking to an unreasonably low return upon the investment, the rental value of the water power for other purposes will probably insure the continuance of a satisfactory return upon the total investment.

Even if it were granted that the "cyanamid" process is prospectively to play the leading role in the fixation of atmospheric nitrogen so far as the most important use of nitrogen is concerned, namely, in agricultural fertilizers, and even if it were further granted that it is the logical source of nitric acid, the question may still be an important one as to whether the raw product of this process may be looked to as the source of a long and important line of nitrogen derivatives. The fact is that there is an almost interminable line of derivatives which can be produced from cyanamid with the greatest technical success and assurance and their manufacture has proved to be in some cases commercially feasible. The direct and valuable application of the raw product, cyanamid, is unique in air nitrogen fixation processes. The proof of this value lies in the fact that fully eighty percent of the entire annual product of normally $15,000,000 value is sold as the raw product.

The principal derivative at the present time is ammonia, which has earlier herein been referred to. None is being made in America at this time outside of the Cyanamid Company's research laboratory, but abroad various plants are producing some fifteen tons of gas per day, part of which goes into high-grade sulphate for fertilizer use and part into anhydrous ammonia. There is also installed and about ready for operation a large Norwegian plant erected for the Birkeland and Eyde interests for transforming some sixty tons of cyanamid per day into ammonia, which will be absorbed in nitric acid for the production of ammonium nitrate. The transformation takes place according to the following reaction:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

This decomposition is accomplished by the use of water and high-pressure steam in autoclaves, and large-scale working plants show an efficiency of over ninety-nine percent nitrogen transformation. The ammonia gas is delivered from the autoclaves mixed with steam and absorbed directly in sulphuric acid without removal of the steam, or passed through a very small ammonia column equipped with condensers and coolers for the removal of the steam, thereby yielding a very high-grade pure ammonia gas. In case it is desired to make anhydrous ammonia it is simply necessary to intensify this drying action and compress the gas; considerable quantities of this ammonia are sold in France in the anhydrous state. The cost of the transformation is almost negligible, as the units have very large capacity and require very little attention.

Cyanamid in the presence of water tends to transform itself slowly to dicyandiamid, and this latter to urea. Methods have been recently evolved which make practicable these transformations either to urea or dicyandiamid with approximately ninety percent efficiency and obtain chemically pure salts as the end product. Dicyandiamid, formula H_2CN_2, contains 66.6 percent nitrogen, or probably the highest concentration of any staple nitrogen compound. It has been proposed for use in explosives, acting as a deterrent, also for use in the dye industry. Its greatest future possibly lies in the ease with which acids transform it into the guanidines, which should find large uses in the explosive industry. The material has been proposed for use as a fertilizer because of its high nitrogen content, but it is probable that its slow decomposition in the soil will never warrant its use for this purpose.

The United States is importing about $50,000 worth of high-grade urea annually for the celluloid industry alone, and could this material be cheaply produced there is no doubt but that it would find an even greater use in the explosive industry. Considerable quantities of this material have been produced in the research laboratory, which has been tried by the celluloid manufacturers with perfect success. It is now practicable to replace the importations of this expensive salt.

In the field of organic derivatives of cyanamid there is practically no end to the series that have developed abroad. The latest addition to this group has been creatin, which seems to be getting somewhere close to synthetic foods.

The calcium in the calcium cyanamid can be replaced by the heavy metals, and recent experimenting with some very interesting compounds, such as lead cyanamid and copper cyanamid, promise valuable results.

When certain grades of cyanamid are melted with common salt the free graphite in the original material is combined with the calcium cyanamid forming cyanide. A transformation of better than ninety percent nitrogen efficiency is obtained and the resulting product contains approximately twenty-five percent KCN equivalent. This material, which can be prepared so as to deliver it into the hands of the consumer at about two-thirds the present price of high-grade cyanides, requires solution in water and filtration. Both operations are easy, and the filtrate can be used in the place of cyanide for the extraction of precious metals. Large scale experiments have been tried out in various cyanide works throughout the world, and in every case it has proved to be identical in behavior with regular cyanide, showing the same extraction efficiencies. The lower price at which this material can be delivered to the consumer more than takes care of the very simple extra dissolving and filtering operations incident to its use, and there should be, therefore, a very large field for this material supplanting the more expensive, high-grade cyanide.

Naturally when the transformation to cyanide is so simple it is also possible to manufacture ferrocyanide, and enter into the case-hardening field and other uses for this material. As a matter of fact, cyanamid itself can be very simply compounded into a case hardener which is the equal of any of the present materials on the market and superior to most of them. The German cyanamid makers have, since the beginning of the war, been swamped with orders for this case-hardening material, sold under the name of "Ferrodur."

Reference has been made heretofore in this paper in a general way to nitric acid production from ammonia. There has been developed recently a new process of re-oxidizing ammonia to nitric acid at high efficiency. It is believed to do away with all of the limitations of the Ostwald process and, if so, the industry will be in a position to meet nitric acid demands by way of cyanamid at a cost under conditions existing in the United States below anything any other process can offer. The gases leaving the oxidizing chambers are many times more concentrated than those from the "arc" process furnaces and, therefore, condensation is greatly simplified and recovery much increased. The units can be made large or small and their cost is rather low, so that small nitric acid plants can be installed at almost any place in the country within shipping range of the cyanamid plant, it being autoclaved into ammonia and converted into nitric acid at the point of use.

Quite recently the American Cyanamid Company has been using the "cyanamid" process as a means of producing argon gas in quantities, producing the nitrogen by means of the copper process and later eliminating the nitrogen by continued re-absorption in the cyanamid ovens leaving argon as the final gas. Thousands of feet of this gas, highly concentrated, is being sold to the lamp industry, chiefly for American use, but in part to consumers abroad at the home of the chemical industry.

THE FIXATION OF ATMOSPHERIC NITROGEN.*

By W. S. LANDIS.

The author assumes that you are all more or less familiar with the use of nitrogen in one or more of its various combinations, for to catalog even a partial list of the most common, commercial nitrogen compounds, would read like pages out of Olsen's Chemical Manual or from the Chemiker Kalender. He is not going to bore you with statistics of consumption of the nitrogen compounds, because the very complex nature of these statistics would make them difficult of comprehension if merely read from prepared tables, and our time can be better occupied along more interesting lines intimately connected to the subject. It is only necessary to add that in tonnage alone the nitrogen compounds stand well at the head of the list in the world's trade in heavy chemicals; nitrate of soda and sulphate of ammonia being produced in 1913 to the value of $200,000,000.

Not including atmospheric nitrogen whose utilization is yet in its infancy, we are practically dependent for our supply of this value element upon the nitrate reposits of Chile, and its recovery as a by-product from coal. The Chilean deposits have been so frequently and fully described elsewhere that we can omit further reference to them. However, the supply of Chilean nitrate is limited and the material can be utilized for only a few purposes, such as in the manufacture of fertilizers and acids.

Ammonia, as a by-product from fuel burned in coke ovens and gas producers, is one of the most valuable forms of combination. This method of recovery will give an ever increasing supply for many centuries to come. This source of supply, however, is somewhat unsatisfactory, because a ton of coal yields only 5 to 6 lbs. of ammonia as a by-product, and by-products have many limitations as a source of primary supply. This is well illustrated by the present status in Germany. There is in that country at present a considerable shortage of nitrogenous fertilizer because the Government has confiscated all stores of nitrate for military purposes. (The fertilizer industry there consumes about 800,000 tons of nitrate per year.) The coke ovens, which we should expect would normally come to the rescue in such a crisis, are, however, largely closed down because industrial Germany is at a standstill, and no one wants coke. Ammonium sulphate production is, therefore, correspondingly decreased just at a time when agriculture needs it most, and its lack is felt acutely. Lately the use of coal is almost prohibited in Germany in order to force the use of coke and thus increase supply of ammonia and tar.

We come very near having the same conditions arising in this country, for were the farmer in position to take his normal fertilizer requirements there would be a great sulphate shortage, as our own industrial depression has closed down many of our coke ovens, and we would have no ready means of meeting even a normal demand for sulphate. We thus see the disadvantage of a by-product source of such an important element as nitrogen, and why inventors have turned so actively to finding a substitute for the Chilean nitrate and the coke-oven ammonia.

Naturally the inexhaustible store of atmospheric nitrogen has presented itself most prominently in this search for a new source. Neglecting the many proposals which have merely wasted much paper and ink in describing impossible methods for the fixation of atmospheric nitrogen, let us devote our attention solely to the successful, and at the present time commercially developed efforts in this field. We can classify these successful attempts into three groups:

1. Direct synthesis of nitrogen and hydrogen to ammonia.
2. Combustion of nitrogen and oxygen in the electric arc.
3. Combustion of nitrogen with metals or carbides.

The only commercial process today belonging to Group 1 is the so-called Haber Process. Dr. Bernthsen described this process at the Eighth International Congress of Applied Chemistry, and exhibited a small working model of the apparatus. I am sorry that I can add but little to the technical information he there presented, but the owners of this process have maintained the greatest secrecy with respect to its commercial development, and but little is known in the commercial world regarding the details.

This process consists in passing a mixture of three volumes of hydrogen and one volume of nitrogen at a pressure of upwards of 150 atmospheres, over a suitable catalyzer operating at a temperature of some 500° to 700° C. A single passage of this mixture through the apparatus causes a transformation of 2 per cent to 6 per cent of the nitrogen to ammonia, which is recovered from the apparatus by condensation, and the rest of the uncombined gases are again returned to the cycle.

Too much honor cannot be shown the courageous chemists who have succeeded in placing this process on a commercial working basis. The difficulties seem almost insurmountable. The catalyzer, which has taken various forms and compounds, principally metals and carbides, poisons very readily, and, therefore, extreme care must be taken in the purification of the gases. Purity which the average chemist would classify as C. P. finds no place in this industry, as that would lack almost as much of meeting the requirements of the process as the use of crude chemicals in the analytical laboratory. It took years of work to find a suitable metallic container for the high pressure gas mixture, because of the permeability of most ordinary materials. However, most of the difficulties have all been overcome, and I have been reliably informed that the Badische Plant at Oppan supplied its allotted quota of sulphate to the German Sulphate Sales Company last year, but I greatly doubt that they did it at a profit if it was made from synthetically produced ammonia, with sulphate prices as low as they were in the early part of 1914.

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*From The American Fertilizer. An address delivered before the Chemical Society of Washington, at Washington, D. C., on Wednesday evening, March 17, 1915, and to the Philadelphia Section of American Chemical Society, at Philadelphia, Pa., on March 18, 1915.

This process as ordinarily understood is not supposed to involve the use of any considerable quantity of electric power, which is not quite true, but does require a large amount of highly skilled labor, for the units are small and complicated. This particularly suits it to the Rhine location, but renders its value in the United States rather questionable. At Oppan, the Badische Anilin Soda Fabrik must dispose of large quantities of waste sulphuric acid, and have by-product hydrogen, hence local conditions favor the process above all others. I personally cannot see a future for its operating under American conditions, particularly in view of the competition of the much cheaper cyanamid process which furnishes the same end product—ammonia.

The second group of processes embrace those oxidizing the nitrogen of the atmosphere in the electric arc. It is well known that when air is heated to temperatures of above 1800° C. and rapidly cooled, the nitrogen oxidizes to NO and remains in that form. At this temperature, however, the reaction velocity is very low and commercial working requires that temperatures of above 3000° C. be used, at which temperature the reaction velocity becomes quite considerable.

Three types of apparatus are in commercial use for performing this reaction:

1. The drum furnace with disc arc, or Birkeland-Eyde.
2. The long tube furnace with spiral arc, of Schönherr.
3. The narrow furnace with fan-shaped arc, of Pauling.

There are numerous other proposed types of apparatus which are claimed to be far superior to the above, as reference to patent literature in particular will show, but the above listed three furnaces are the only ones in actual every-day operation.

The products obtained by passing air through the arc of any of these furnaces consists of a highly heated gas containing from 1 to 3 volume per cent of nitric oxide. On cooling down to temperature of approximately 600° C. this nitric oxide unites with free oxygen to form nitrogen peroxide NO_2; on further cooling of this nitrogen peroxide to below 140° C. it polymerizes to N_2O_4. When brought into contact with water and oxygen, this reacts, forming a mixture of equal molecular parts of nitric and nitrous acids. By subjecting the nitrous acid to further action of the peroxide this is also changed to nitric acid with the liberation of nitric oxide, which again passes through the cycle. Thus by suitable cooling of the nitric oxide in the presence of air and water, one ultimately attains a product which consists almost quantitatively of nitric acid, and actual operating results of the large furnace plants have shown a steady recovery of about 90 per cent of the nitrogen oxides in the form of nitric acid or nitrate salts, the remainder being recovered as nitrate or not absorbed.

In general the handling of the nitrous gases from the arc furnace is now well standardized, and the design of a condensation plant is almost as well understood today as that of a sulphuric acid plant. After passing the various systems of cooling apparatus, consisting of steam boilers, evaporators, etc., the gases enter aluminum condensers where the temperature is reduced to approximately 100° C. They then enter a preliminary oxidation chamber so proportioned that they remain in the same at least 1½ minutes before leaving, where the preliminary oxidation to peroxide takes place. The gases next pass into a series of four or five stoneware or granite towers where they are washed with water by a counter current system, remaining in the tower system for from three to five minutes. Of the nitrogen oxidized, 90 per cent is here condensed as nitric acid, the most concentrated acid being obtained in the first tower, and averaging from 30 per cent to 35 per cent HNO_3. After passing these condensing towers, the gases usually enter a final tower fed with caustic soda liquor, where a further 3 per cent to 5 per cent of the oxidized nitrogen is recovered as sodium nitrite. The remaining 5 per cent passes out into the air unabsorbed.

As above mentioned, these towers deliver a 30 per cent to 35 per cent nitric acid; this can be further concentrated to 50 per cent nitric acid, using the heat of the hot gases issuing from the arc furnace to perform the necessary evaporation. It is not possible to carry this evaporation much above 50 per cent for economical reasons, and where higher concentration of nitric acid is demanded special complicated concentration processes must be employed.

Dilute nitric acid, as obtained from the towers, finds little use in industrial processes, and it is difficult to transport. Most of the nitric acid plants, therefore, either concentrate it to 96 per cent acid by special means, or convert it into calcium nitrate for fertilizer use, or into ammonium nitrate for explosive purposes. In the latter case most of the ammonia used today in the nitric acid plants, operating on the arc system, is obtained from cyanamid. It is quite probable that calcium nitrate will soon disappear from the fertilizer market as it certainly cannot be sold at a profit in competition with Chilean nitrate or ammonium sulphate, even when the latter is made from cyanamid.

As we shall see later, these arc processes require enormous quantities of cheap electric energy, and must be located near such power centers. We have no cheap power in the United States, and there is no immediate prospect of our having an arc process in continuous large scale operation within our borders. Our Western powers are far from markets and transportation of nitric acid to the East is almost out of the question.

The third group of processes embraces fixing nitrogen by metals or carbides, and has reached its highest development in the cyanamid process, which last year produced throughout the world in the fourteen factories at present operating, some 300,000 tons of material, carrying over 20 per cent nitrogen.

The inventors of the cyanamid process originally attempted the synthesis of cyanides by subjecting barium carbide to the action of nitrogen, which, as is well known, forms barium cyanide. On attempting to use the cheaper calcium carbide in place of barium carbide, Doctors Frank and Caro found that instead of obtaining cyanide they obtained a new material, which proved to be calcium cyanamid. It was later found that this material could be utilized directly in agriculture, and from this discovery has grown the enormous industry, which has proved to be the cheapest source of fixed atmospheric nitrogen at present in existence.

Reference to the literature existing upon the manufacture of cyanamid seems to lead one to suppose that it is a comparatively simple matter to carry out the reaction so frequently written:

$$CaC_2 + N_2 = CaCN_2 + C.$$

This might be true to a limited extent were this the only action to contend with, but even this reaction itself is so complicated that while it is well known that it is reversible, no one has yet succeeded in correctly establishing its equilibrium constants. A laboratory study of this reaction has been carried out both in this country by Professor Thompson and abroad by Professor Haber, but neither of them has succeeded in mastering the same, because of the peculiar difficulties that arise in a study of it.

Naturally, if the highly skilled chemical laboratories met with these difficulties, we can assume that practice runs against a few of them itself. But side from the fundamental absorption reaction, as written above, there are a number of other complications that arise in this industry, which we meet with in our every-day work.

The fertilizer industry, into which most of our material at present goes, is a rather peculiar one, and probably has more peculiar fads and precedents than almost any other highly developed industry in the country. Naturally, to sell them material, one must take into account all of the peculiarities of this industry, and must meet them, a fact which further complicates the cyanamid industry itself. You can assume that inasmuch as cyanamid is being produced and sold at the rate previously mentioned we have succeeded in meeting the requirements.

The first stage of the cyanamid process involves the production of calcium carbide. To produce, day after day, a high-grade calcium carbide that meets the peculiar requirements of the cyanamid industry, is quite an art in itself. There are no journeymen carbide workmen in our country, and we had to start out and develop our own furnaces and methods of operation. We had to seek sources of raw materials for this manufacture which are quite different from those which meet the requirements of lighting carbide, and we have to operate our furnaces in a certain peculiar way in order to combine these raw materials into a product of such structure and grade that we can make cyanamid out of it successfully. As you will recall, Moissan in his early work found that he could nitrify only certain kinds of carbide, showing that there are conditions existing in our carbide manufacture that are different from those in the manufacture of lighting carbide.

Our next great problem was to grind this special grade of calcium carbide so that it passes a hundred mesh screen. Naturally, this must be done without slaking the carbide, as hydrated lime does not make cyanamid. Now 100-mesh carbide dust, when exposed to the atmosphere on a damp day, or thrown out on damp ground, is almost as explosive as low grade dynamite, so that it is quite a problem of itself to grind this carbide to the required degree of fineness.

Next comes the production of nitrogen. It is a comparatively simple matter for the chemist to make a few cubic centimeters of high grade nitrogen in his laboratory, but if one were to call upon him for two million cubic feet of a practically pure nitrogen per day, such as we make at Niagara, he would probably have to do considerable research to find out just how this enormous quantity of such high grade material could be made. In the early days of the cyanamid process, when the Niagara plant started, liquid air machinery was in a rather backward state of development, and we were forced to make our nitrogen by passing air over copper. The original plant was later enlarged. It was a long step from the combustion tube of the chemical laboratory to our present plant using retorts containing 5 tons of copper mass, but it has been successfully solved, and the new plant has been in operation with a minimum of trouble for some years. In the early days of the industry at Niagara, we could draw upon natural gas for reducing the copper oxide, so as to revivify it, but this gas supply has since failed, and we were forced to put up our own coal gas plant. Even this coal gas plant is not a standard one, inasmuch as we are coking coal, not only for the production of gas, but also to furnish the coke for our carbide furnaces. We are running at temperatures in our retorts, and obtaining qualities of coke and gas that the average city gas plant would not consider possible of attainment.

Eventually, we had to install purification apparatus for taking out the impurities in the nitrogen, as it came from the copper retorts, and have installed soda towers for removal of carbon dioxide, refrigeration plants for drying, lime tanks for purification, etc., and have even included a causticizing plant for recovery of our spent alkali.

After the development of the liquid air machinery, both in the way of capacity and reliability, the problem of producing pure nitrogen was much simplified, and our latest addition at Niagara includes what was probably the largest liquid air plant in the world at the time it was built, a year ago. This plant alone throws to waste almost thirty gallons of liquid air an hour, just to keep the apparatus flushed out and in good working order.

After one has overcome the difficulties in the production of a proper grade of nitrogen and of carbide, the next step is exposing these two to mutual reaction at a proper temperature, which is done in small individual ovens, holding from one-half to two and a half tons of carbide. This reaction itself is reversible and particular precautions must be taken to keep it always running in the right direction until the carbide has all been nitrified.

The product removed from these ovens is a black, hard cake, which analyzes 22 per cent nitrogen, and about 1 per cent unnitrified carbide. This material, which we call lime-nitrogen, is next finely ground and stored in silos. The carbon set free in the reaction above indicated is in the form of graphite, and it is not an easy proposition to find a satisfactory mill that will grind the material fine and at the same time not blow itself up from liberated acetylene derived from the presence of any uncombined carbide, or wear itself out grinding the lime-nitrogen-graphite mixture. Extreme precautions are taken in this part of our operation, both in the mills themselves and in the elevating and conveying apparatus connected with them to avoid dangerous explosions. Thus far, not a single injury has resulted from such explosions in the cyanamid plant.

To prepare the lime nitrogen for agricultural purposes the finely ground material is partly hydrated to insure decomposition of the carbide it contains, and is then oiled to render it dustless and is stored in bulk, or packed immediately into sacks and shipped to the fertilizer mixer.

Agricultural uses, however, are not the only purposes to which the cyanamid can be applied, as it is a very simple matter to convert the cyanamid into ammonia by the exothermic reaction—

$$CaCN_2 + 3H_2O = 2NH_3 + CaCO_3.$$

If lime nitrogen is mixed in a slurry with water and subjected to the action of heat and high pressure, it is converted quantitatively into ammonia. In this country the use of cyanamid was not developed on a large scale outside our experimental laboratory until the beginning of this year, but while I was in Germany recently, I saw in the yards of a big manufacturing concern there some 60 autoclaves, each capable of converting 10 tons of cyanamid into ammonia per day. This equipment was awaiting railroad cars to move it out, and was in no sense experimental, because three similar plants have been in operation in Germany for at least three years. The cost of this transformation is not appreciable, and the purity of the product is quite high, requiring merely passing through a rectifying column for removal of steam.

The ammonia abroad is at present being converted into a high grade sulphate and a pure nitrate, and we are at work now in this country on producing a new fertilizer material, "Ammo-Phos," consisting largely of ammonium phosphate. This product contains over 13 per cent NH_3, and 45 to 50 per cent P_2O_5, or over 60 per cent plant food, most of the remainder being chemically combined water. When mixed with the high-grade potash salts, it will make a complete fertilizer three to four times as concentrated as the average grades sold today.

It is also possible to transform cyanamid into urea and we have made in our experimental laboratory a considerable quantity of very pure urea.

Similarly, cyanamid can be converted into dicyandiamid by treatment with water at 90° C. This material has been proposed for use as a deterrent in explosives, but I think offers a much better field for transformation into guanidines.

These transformations of cyanamid have received a great deal of attention abroad and there are numerous derivatives on the market. Just a few months ago, I saw a sample of creatin which had been made in a chemical laboratory from cyanamid, an achievement that is not very far from the synthetic production of foods.

When a special grade of cyanamid is melted down with a flux, such as common salt, it combines the free carbon present with the cyanamid radicle, forming cyanide. The resulting product of this fusion contains about 25 per cent of its weight in equivalent potassium cyanide; this crude form of cyanide dissolves very rapidly in water and filters rapidly from this insoluble, after which the solution is ready for metal extraction, or other uses to which cyanide in its dissolved form can be put. Large scale experiments have been tried out in a number of big cyanide plants scattered at various places throughout the world, and in every respect this material has shown an exact equivalent value to the higher grade cyanides. The transformation of the cyanamid nitrogen into cyanide nitrogen is almost quantitative, and the fusion experiments can be carried out without difficulty, and at a low cost. We have here, therefore, a crude form of cyanide which can be prepared very cheaply and which could be readily delivered to the consumer at a price approximately one-third under the present prices of the higher grade cyanide. Abroad this material has been made in large quantities and transformed into pure cyanide running approximately 127 per cent potassium cyanide equivalent.

Cyanamid itself forms an excellent case hardening material, and we have prepared a number of mixtures which are in steady use at our plant for performing this operation upon various machine parts which we are using. It works rapidly and at a low temperature, but we have not yet succeeded in overcoming certain fads in large scale use of this material, and it has not met with any general introduction. We found that the case hardener is usually more concerned with the color of his hardening powder than he is with the actual work it performs and as the colors and odors of our cyanamid products are rather fast, we have not found it interesting to meet some of these peculiarities of the case hardening trade. While abroad, I saw these case hardening materials being prepared by the hundreds of tons for use in preparing armament and war materials, and the small factory engaged in their production has been swamped with orders ever since its inception.

The arc processes have shown themselves capable of producing nitric acid or nitrates; cyanamid itself is an entirely different product, and there has recently been evolved abroad a most successful method of oxidizing this ammonia to nitric acid, so that in case of competition with the Birkeland-Eyde process, we are not entirely limited to the fixation of nitrogen, but can furnish this nitrogen in exactly the same form that their process can, and at considerably less cost. Our raw materials are cheap—coke, limestone, air. We use only one-fifth of the electrical power that the arc processes do per unit of nitrogen fixed in the form of cyanamid, in respect to ammonia, and by the addition of a very small percentage more power we can convert our cyanamid into nitric acid. We require about the same quantity of labor to fix a unit of nitrogen in cyanamid as the arc process does in nitric acid, but since there is only a small fraction more labor used to transform cyanamid nitrogen into nitric acid, we do not feel this is a great handicap when one considers our lower power consumption. On the American continent where water powers are so expensive and so scarce this difference readily offsets the additional labor necessary to make nitric acid from cyanamid. Further, our cyanamid is easily transported and can be changed to ammonia or nitric acid at the end of its journey at the expenditure of a small amount of steam and labor, so that we have the additional advantage in transportability of stable raw material, and subsequent conversion at the point of direct use. These commercial transformation untis are small, and can easily be set up to supply even small amounts of ammonia or acid in a quite cheap and efficient plant.

There is no comparison between the initial investment required for a cyanamid plant and for an arc plant if one will include power development. The cyanamid plant per unit of nitrogen fixed, requires an investment of only one-fourth that required by the arc process, and for a cyanamid-ammonia plant about one-half that required by the Haber process. Even the combination of the cyanamid-ammonia-nitric acid process requires an investment of only one-third to one-half that for the arc process. In each case we are assuming exactly the same quantity of fixed nitrogen in the forms above designated. Where electrical power is expensive, as in the United States, there is no question regarding the superiority of the cyanamid process for the fixing of atmospheric nitrogen, particularly for fertilzer purposes, and we eventually hope that the future development of our nitric acid process will enable us to compete in every line of nitrogen compounds with all other competitive sources.

STANDARD SPECIFICATION FOR SOAP.

Upon the recommendation of the Director of the Bureau of Standards, the Secretary of Commerce addressed the following letter, dated April 14, 1915, to the heads of the various executive departments and independent Government establishments, relative to drawing up a United States standard set of specifications for soap materials:

This department has received communications from soap manufacturers stating that they have refused to bid on certain Government proposals for soap materials on account of the exceptional nature of the Government specifications.

Without going into the merits or demerits of any particular specification, it does appear that there is a certain justice in the criticism, since in the General Supply Schedule about 20 different kinds of soap and detergent materials are called for, and, in addition, many Government branches have other specifications. While no positive number can be stated, it is probable that there are altogether as many as 30 to 40 different specifications issued by the Government for this class of material, and it is also very probable that with proper co-operation the total number could be reduced to less than 10, and that definite specifications could be drawn which would secure better and cheaper material than is now purchased.

With this object in view, you are requested to appoint a representative who is thoroughly familiar with the needs of your office and authorized to act for it to co-operate with the Bureau of Standards in drawing up a United States standard set of specifications for this type of materials. After getting the views of the representatives of the various branches of the Government it is proposed that the committee consult the most prominent manufacturers before finally agreeing on any set of specifications.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Written for the Chemical Engineer.

Analysis of Paint.

The analysis of paint is usually a somewhat complicated process, but the complications can be reduced to a minimum by keeping in mind the material that is likely to be present in a paint, and by making the qualitative examination of the material before the quantitative examination is begun.

It will doubtless be of assistance to the analyst to have presented in tabular form the constituents commonly found in a white paint, and in some of the most common colored paints.

The general constituents in the white paints are white lead or basic carbonate of lead, zinc white or zinc oxide, sublimed white lead, or basic lead sulphate, and lithopone, which is a mixture of barium sulphate and zinc sulphide in molecular proportions. In addition to these major constituents there are also certain inert white pigments, which should be included in the examination. These are barium sulphate, barium carbonate, calcium carbonate, calcium sulphate, china clay, silica, and asbestine or magnesium silicate.

The chief coloring materials which are likely to be mixed with these whites for the production of a colored paint, are as follows: For the browns and yellows we find the ochres, umbers and siennas together with the lead chromate and basic lead chromate. For the reds and dark browns we usually find some of the oxides of iron, such as natural ferric oxide, and artificial ferric oxide, hydrated ferric oxide, etc. Also among the orange and red pigments we find the oxides of lead Pb_3O_4, which is read, PbO_2, which is brown, and PbO, which is yellow. A mixture of these oxides in various proportions will make up different shades from red through orange to a light yellow. The blue pigments are primarily ultramarine blue and Prussian blue. There is only one green pigment used to any extent, which is chrome green, consisting of a mixture of Prussian blue and chrome yellow. The black pigments are primarily carbon compounds such as bone black, drop black, ivory black, lamp black, mineral black and graphite.

The analysis first to be described will be that applicable to a mixed white paint, and following this will be given the methods of estimating the constituents which may be present in a colored paint. It is of course understood that in a colored paint all of the constituents of a mixed white paint will be present, plus the material which imparts the color.

The first procedure in the treatment of a mixed paint will be the separation of the paint from the vehicle. This can best be accomplished by weighing out say 50 grams of the paint in a conical glass centrifuge bottle, stirring it up thoroughly with about 100 c.c. of a mixture of 50 parts benzole, 40 parts methyl alcohol, 10 parts acetone. The bottle is then centrifuged for 15 to 20 minutes. The liquid is then poured off from the sediment. Another portion of solvent stirred up and again centrifuged. The pigment is removed from the conical container to a watch glass and weighed. From this weight is calculated the per cent pigment and the per cent vehicle in a paint. The dried pigment is then ready for analysis.

Qualitative Analysis.—In the majority of cases a complete qualitative analysis of the pigments present is hardly worth the time it requires, as there is but little time lost in following the regular quantitative scheme. If, however, a qualitative analysis is desired, the following outline will be found sufficient in most instances, the removal of the vehicle previous to these tests being understood.

Carbonates.—Effervescence with concentrated hydrochloric acid indicates carbonates, or hydrogen sulphide if zinc sulphide be present, the latter being distinguished by its odor and by the fumes blackening a piece of filter paper moistened with lead acetate.

Barytes, Silica, Clay, or Other Silicates.—Boil above mixture 5 minutes, dilute with boiling water, filter. An insoluble residue may be barytes, silica, clay, or other silicates. Test for barytes with flame test, using a platinum wire. A characteristic green color indicates barium.

Sulphates.—Test a small portion of the acid filtrate for combined sulphuric acid with a few drops of barium chloride.

Lead.—Test another small portion of the acid filtrate with sulphuric acid. A white precipitate at once or on standing indicates lead.

Zinc.—Take another small portion of the acid filtrate and add a few drops of potassium ferrocyanide. A white precipitate with a bluish tinge indicates zinc.

Calcium.—The remaining portion of the acid filtrate is made alkaline with ammonia and hydrogen sulphide passed in for five minutes. Filter and test filtrate for calcium with ammonium oxalate, setting aside in a warm place.

Magnesium.—After completely precipitating the calcium add a few drops of hydrogen sodium phosphate. A precipitate on standing indicates the presence of magnesium compounds.

The identification of the forms in which the lead may occur can only be determined by the quantitative scheme if both sulphate and carbonate are present.

QUANTITATIVE ANALYSIS OF WHITE PAINT.

Total Lead.—Weigh 1 gram of the dry pigment into a 250 c.c. beaker. Add 30 c.c. of strong hydrochloric acid, boil 5 minutes, add 50 c.c. of hot water, heat 15 minutes longer, settle, filter while hot, and wash thoroughly with boiling water. The washing should be begun the instant the solution has filtered through, in order to avoid any crystallization of lead chloride in the pores of the filter paper. Once formed the crystals can only be dissolved with difficulty and with the use of an excess of wash water, which, as stated, must be at boiling temperature. This operation is best conducted by the aid of suction. Casein and other products of a similar nature are occasionally used in the manufacture of mixed paints in considerable quantities, and the analyst should always be on the lookout for the possible presence of these substances.

The solution is made just alkaline with ammonia, then just acid to litmus with hydrochloric acid. It is very necessary that the solution be only barely acid, as a comparatively small quantity of free acid will keep considerable lead from precipitating. Having been made barely alkaline, which is indicated by the precipitation of the lead, the solution is brought to a faintly acid condition by using dilute hydrochloric acid (1 to 10). Dilute to about 350 c.c. Cool, pass in hydrogen sulphide gas, noting the color of the precipitate; if gray, some zinc is being thrown down; if reddish black, the solution is too acid. Add a few drops of dilute acid or ammonia as the case requires. Settle, filter and wash with cold water.

Place filter and precipitate in 25 c.c. of nitric acid and 25 c.c. of water, heat gently until the lead has all dissolved, as shown by the residual sulphur having a yellow to whitish color. Do not boil hard enough to thoroughly disintegrate the filter paper. If difficulty is experienced in dissolving the lead contained in the sulphur particles, it is better to collect them into a ball with the aid of a stirring rod and remove to a small beaker and treat with a few cubic centimeters concentrated nitric acid, and heat until dissolved, then pour back into the larger beaker.

Pour solution and filter paper on to a suction funnel provided with a platinum cone. If any fine particles pass through, pour the filtrate back again. This procedure permits the washing of the filter mass with a very small amount of water, thus saving considerable time in the subsequent evaporation. Add 5 c.c. of dilute sulphuric acid to filtrate, and evaporate until sulphur trioxide fumes appear. Cool, add 25 c.c. of water, 25 c.c. of alcohol; allow to stand one-half hour with occasional stirring; filter using Gooch crucible, wash with dilute alcohol, dry, heat gently over ordinary lamp, and weigh as lead sulphate.

Calcium.—The filtrate containing the zinc, calcium, and possibly magnesium is made slightly alkaline with ammonia, a few drops of mercuric chloride, solution (1 to 10) added, and a steam of hydrogen sulphide gas passed into the solution for about 10 minutes.

The addition of the mercuric chloride renders the precipitate granular and very easy to filter, and entirely obviates the difficulty of filtering a slimy zinc sulphide precipitate. In the analysis of tints where the zinc cannot be titrated until it has been freed from iron, the addition of the mercuric chloride will not cause any trouble, as treatment with hydrochloric acid results in the solution of the zinc only, the mercuric sulphide being insoluble in hydrochloric acid. Settle, decant, filter, and wash.

Evaporate the filtrate from above precipitate to about 150 c.c., make alkaline with ammonia, add ammonium oxalate (50 c.c. for 1 gram of lime) usually 20 c.c. is sufficient and set in a warm place for two or three hours. Fliter, wash, ignite, and weigh as calcium oxide, or titrate precipitate with permanganate by placing filter and the thoroughly wash precipitate in a 400 c.c. beaker, adding 200 c.c. of boiling water and 25 c.c. of dilute sulphuric acid, and titrate with standard tenth-normal potassium permanganate.

1 c.c. tenth-normal permanganate = 0.0028 gram CaO.

1 c.c. tenth-normal permanganate = 0.0050 gram $CaCO_3$.

Barium carbonate is still to be found in certain mixed paints, and it is advisable to test for the presence of soluble barium with a few drops of sulphuric acid before precipitating the calcium.

Magnesium.—The filtrate from the calcium oxalate should be tested for magnesium by treating with hydrogen sodium phosphate. Allow to stand one-half hour, and 25 c.c. of ammonia, allow to stand one hour, then filter on to a Gooch crucible, wash with dilute ammonia, ignite, and weigh.

Weight precipitate X 0.7575 = weight magnesium carbonate.

Zinc Oxide—Reagents—Standard Zinc Solution.—Dissolve 10 grams of chemically pure zinc in hydrochloric acid in a graduated liter flask, add 50 grams of ammonium chloride, and make up to 1 liter.

1 c.c. = 0.01 gram, zinc or 0.01245 gram zinc oxide.

Standard potassium ferrocyanide solution. Dissolve 46 to 48 grams of crystallized potassium ferrocyanide in water make to 1.000 c.c.

Uranium Nitrate Solution.—Dissolve 15 grams of uranium nitrate in 100 c.c. of water.

Standardizing the Ferrocyanide Solution.—To determine the value of the potassium ferrocyanide solution pipette 25 c.c. of the zinc solution into a 400 c.c. beaker. Dilute somewhat and make faintly alkaline with ammonia, bring to a faintly acid condition with hydrochloric acid, and then add 3 c.c. excess of the concentrated acid, dilute to a total volume of about 250 c.c., heat to 80° C., and titrate as follows: Pour off about 10 c.c. of the zinc solution into a small beaker and set aside, run the ferrocyanide into the remainder from a burette, a few cubic centimeters at a time, until the solution takes on a slight ash-gray color, or until the drop of solution placed in contact with a drop of the uranium nitrate solution on a porcelain plate turns to a distinct brownish color. Often the end point has been passed by quite a little.

The 10 c.c. of zinc solution that has been reserved is now added, the titration continued, drop by drop, testing a drop of the solution carefully on the porcelain plate after each addition of ferrocyanide solution. Some little time is required for the test drop to change color, so that the end point may have been passed slightly. This may be corrected for by making a memorandum of the burette readings, having the test drops arranged in regular order and taking as the proper reading the one first showing a distinct brownish tinge. Having noted the number of cubic centimeters of ferrocyanide required for the titration of the standard zinc solution, the value of 1 c.c. may be readily calculated.

Titration of Sample.—One-half gram of the sample if high in zinc, or 1 gram, if the zinc content is fairly low, or the zinc sulphide precipitate obtained in section 310, is dissolved in a covered beaker in 10 c.c. of hydrochloric acid and 10 c.c. of water, the solution diluted and treated exactly as described above for the standard zinc solution, care being taken to titrate to exactly the same depth of color on the porcelain test plate. If the method is carefully carried out, the procedure being uniformly the same in each determination, the results will be found satisfactorily accurate.

Lead Sulphate.—Dissolve 0.5 gram in water, 25 c.c. hydrochloric acid in light excess. Dilute to 200 c.c. and add a piece of aluminum foil which about covers the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, ignite, and weigh as barium sulphate. Calculate to lead sulphate by multiplying by 1.3 as a factor, unless calcium sulphate is present, in which case it is advisable to make use of Thompson's separation.

In the absence of barium sulphate the combined sulphuric acid may be estimated by H. Mannhardt's method: Grind 1 gram of pigment with 1 gram of sodium carbonate very intimately in an agate mortar. Boil gently for ten minutes, the combined sulphuric acid, and in the case of colors containing chromates the chromic acid will pass into solution and may be estimated in the filtrate in the usual manner. If necessary collect the insoluble portion on a filter, dry, detach, and titrate a second time.

Basic Carbonates of Lead (White Lead).—After deducting the amount of lead present in the pigment as sulphate of lead, calculate the rest of the lead as white lead by multiplying the remaining sulphate by 0.852, unless sublimed lead is suspected to be present in which case the combined lead oxide must be taken into consideration.

Insoluble Residue.—The insoluble residue from the original hydrochloric acid treatment may contain barytes, magnesium silicate, silica, and clay. Ignite filter paper and residue until white, weigh as total insoluble matter; grind in agate mortar with about 10 times its weight of sodium carbonate, fuse for 1 hour in a platinum crucible and dissolve out in hot water.

Barium Sulphate.—The solution from the fusion is filtered. The residue consists of barium carbonate, magnesium carbonate, etc., and is washed with hot water. The filtrate and washings are saved. Pierce filter paper and wash precipitate into clean beaker with hot dilute hydrochloric acid; finish washing with hot water, heat to boiling, add 10 c.c. of dilute sulphuric acid to precipitate barium, filter, ignite, and weigh as barium sulphate.

Silica.—The filtrate from the barium sulphate is added with care to the filtrate referred to in the preceding paragraph, making distinctly acid: evaporate to complete dryness, cool, add 15 c.c. of hydrochloric acid, heat to boiling, cool, settle, filter, ignite, and weigh as silica.

Alumina.—The filtrate from the silica will contain all of the alumina except that which was dissolved in the original treatment with hydrochloric acid. This is quite constant, varying from .004 to .005 gram per gram of clay. The acid filtrates are made slightly alkaline with ammonia, and boil until odor disappears. Settle, filter, wash, ignite, and weigh as alumina.

Weight alumina x 2.5372 = weight clay.

Weight clay x .4667 = weight of silica in clay.

Any difference greater than 5 per cent may be considered as free or added silica, according to Scott.

Calcium and Magnesium Oxides.—If qualitative test shows presence of magnesium in insoluble residue from the first hydrochloric acid treatment it was present probably as magnesium silicate. Treat filtrate from the aluminum hydroxide for calcium and magnesium oxides. Magnesium silicate contains 3 to 5 per cent combined water.

Hydrofluoric Acid Treatment.—Instead of restoring to fusion with sodium carbonate the insoluble residue, which should be weighed up in a clean platinum crucible, may be treated with several drops of pure concentrated hydrofluoric acid and sulphuric acid and heated gently on a sand bath under the hood, using only sufficient heat slowly to volatilize the silica and sulphuric acid. Dissolve out in water acidulated with hydrochloric acid. The residue, which is barium sulphate, is filtered off and estimated as such. The filtrate will contain any aluminum, calcium, and magnesium, present which may be estimated and calculated as oxides as above described. The combined weight of the barium sulphate, alumina, calcium and magnesium oxides subtracted from the weight of the insoluble residue used gives the weight of silica. This operation is much shorter than resorting to a fusion and equally as accurate.

Mixed Carbonates and Sulphates.—Occasionally paints are met with which contain calcium sulphate, calcium carbonate, sulphate of lead, and white lead (basic carbonate lead, in which case it is necessary to make a separation of the calcium compounds, which may be effected by Thompson's method as follows:

To 1 gram of the sample are added 20 c.c. of a mixture of nine parts alcohol (95 per cent) and one part of concentrated nitric acid. Stir, and allow to stand 20 minutes. Decant on a filter and repeat the treatment with the acid-alcohol mixture four times, allowing it to stand each time before decanting. The calcium carbonate will go into solution, while the calcium sulphate or gypsum remains undissolved. Add filter and contents to the residue remaining in the beaker; dissolve in hydrochloric acid with sufficient water to insure the solution of the calcium. Make alkaline with ammonia, pass in hydrogen sulphide for 10 minutes, boil, settle, filter. The filtrate and washings are concentrated to about 150 c.c. and the calcium precipitate with ammonium oxalate in the usual manner. The ignited precipitate is calculated to hydrated calcium sulphate.

Estimation of carbon dioxide in the presence of zinc sulphide. This method, devised by Mannhardt, is often useful in determining complex mixtures of pigments. One gram of the pigment is ground for several minutes in a smooth glass mortar with an excess of bichromate of potash, using considerable pressure; the mixture is then placed in the carbon dioxide generator and the carbon dioxide liberated and estimated in the usual manner.

Calculations.—The ignited precipitate of calcium oxide obtained from the portion insoluble in the acid alcohol mixture is subtracted from the total calcium weighed as oxide; the remaining calcium oxide is calculated to calcium carbonate. The total carbon dioxide is determined in a portion of the sample, the portion due to the calcium carbonate is deducted from the total amount, and the remainder calculated to basic carbonate of lead. The combined sulphuric acid due to the sulphate of lime deducted from the total combined sulphuric acid, and the remainder calculated to sulphate of lead.

Wt. calcium oxide X 3.0715 = hydrated calcium sulphate.

Wt. calcium oxide 1.784 = calcium carbonate.

Wt. calcium carbonate X 0.440 = carbon dioxide.

Wt. carbon dioxide 8.8068 = basic carbonate of lead.

Wt. of hydrated sulphate of lime X 0.4561 = combined sulphuric acid.

Wt. of combined sulphuric acid X 3.788 = sulphate of lead.

(To be continued.)

DETERMINING TOTAL SULPHUR IN RUBBER.

In order to learn whether or not the methods recently published for the determination of sulphur in rubber were any improvement over the Waters and Tuttle method, the one now in use at the Bureau of Standards, Department of Commerce, that bureau has made a study of the methods and has published the results of the study in Technologic Paper No. 45, just issued.

The methods investigated were those of Spence and Young, Deussen, Alexander, the Joint Rubber Insulation Committee, Kaye and Sharp, Frank and Marckwald, and Waters and Tuttle. These were subdivided, according to the method of attack, into three classes: Direct solution, direct fusion, and solution and fusion methods. A large number of determinations were made on a number of samples, two of the latter being of known composition which were specially prepared at the Bureau of Standards.

The methods which have been compared may be divided into two classes, viz., those for the determination of the total sulphur and those for the determination of sulphur other than that present in the insoluble sulphates. It was found that the methods of the second class could not be relied upon to give accurate results.

The direct solution methods, those of Spence and Young and Deussen, involve the use of concentrated nitric acid. This was first suggested by Henriques, but is objectionable because it gives rise to low results.

The direct fusion methods, those of Alexander, the Joint Rubber Insulation Committee, and Kaye and Sharp, are reliable only when the free sulphur content is low, and are therefore not applicable to routine analysis.

The solution and fusion method of Frank and Marckwald was found to be unreliable when the free sulphur was high. The Waters and Tuttle method was found to give satisfactory results and recommended for general use.

A new suggestion is offered, namely, to determine separately the free sulphur and the sulphur remaining after the extraction, reporting the sum of the two quantities as the total sulphur. This procedure eliminates the troublesome effect of the free sulphur upon the determination of the total sulphur.

METALLURGY

TITANIUM AND ITS EFFECTS ON STEEL.*

By GEO. F. COMSTOCK.

Titanium is widely distributed in the earth's crust in small quantities and is always found as an oxide, its principal ores being rutile, the fairly pure dioxide and ilmenite, a mixture of iron and titanium oxides. One of its chief peculiarities is the readiness with which it combines with nitrogen. It is one of the very few elements which will "burn" in an atmosphere of nitrogen. Its dioxide is one of the most stable compounds known, and great energy is required to decompose it. Thus it follows that when titanium is separated from its oxygen, it will readily recombine with it, with evolution of heat. The value of titanium in the steel industry is due largely to the fact that its dioxide is so much more stable than iron oxide that its action in "deoxidizing" melted steel is very powerful.

The reduction of the natural oxides is effected either by reduction with carbon by means of the electric arc, or by an alumino-thermic reaction. The former process delivers the titanium in the form of the carbide, while the latter produces an alloy of titanium, aluminum, and iron. The carbide is the form most generally used.

Metallic titanium when heated to redness in nitrogen forms titanium nitride, but when heated in air only the oxide is formed. The nitride is slowly converted to the oxide when heated to redness in air, but the carbide burns vigorously in air, forming dioxide. The reverse reaction takes place only at very high temperatures. Even at the temperature of the blast furnace titaniferous ores do not give more than 1 per cent of titanium in the pig iron. This is probably present partly as carbide and partly as cyanonitride. Although in the blast furnace titanium nitride is sometimes formed, it is not present in the titanium-carbide alloy used in treating steel, for at the temperature of the electric arc furnace, in which this alloy is made, with a reducing atmosphere and excess carbon the nitride is dissociated in favor of the carbide.

For general effectiveness titanium is the best of the various deoxidizers for steel. The carbide gives results quite as good as the pure metal and is much cheaper. A material is sold at 8 cts. per pound containing 15 to 20 per cent Ti, and known as "Ferro Carbon-Titanium." It consists of microscopic particles of titanium carbide held in a matrix similar to gray cast iron. When added to melted steel the matrix dissolves quickly, and the particles of titanium carbide are rapidly diffused through the bath, where they react vigorously on the oxygen.

The aluminothermic alloy, which contains very little carbon, is an alloy of aluminum and titanium in iron, and hence its use involves the production of the effects of both these elements. The chief objection to its use is the harmful effect of aluminum in hindering the removal of oxide and slag enclosures.

Titanium oxide acts as a flux for silicates and other slags that may be in the steel. The best cleansing action is obtained when the titanium is added without aluminum, or in the form of the carbide rather than as the aluminothermic alloy. The latter should only be used in the few rare cases where the addition of the carbon of the alloy would be undesirable. In soft steels the increase in carbon from this addition would not be more than about 0.01 per cent, so that the cases where this would make any material difference are very few indeed. Practically all the titanium used in steel in America at the present time is in the form of ferro carbon titanium, a large percentage being used for rail steel, although its use in other steels is growing steadily.

"Titanium steel," properly speaking, is not made commercially at present. Such a title naturally implies a steel whose properties are dependent to an appreciable extent on a certain content of titanium. The advantages of the titanium-treated steels as made today are due to greater soundness, cleanness, and less segregation, and not, as far as is known at present, to the small amount of titanium left in the metal. In no case has over 0.025 per cent of titanium been found in any sample of titanium-treated steel analyzed at our laboratories. It is very difficult to make steel absorb more than 0.025 per cent titanium under the usual conditions of manufacture, and no use has yet been found for steel containing larger quantities that would warrant the attempt to produce commercially a real "titanium steel."

Steels made by the Bessemer, open-hearth, or crucible processes are treated with titanium, but most of this element is used in open-hearth steel. The alloy is furnished in various sizes, from lumps of about 1 in. diameter to powder, according to the quantity of steel to be treated at one time, and for the best results it must be added to the melted steel as it flows from the furnace to the ladle. After the addition the steel must be kept in the ladle for from 3 to 10 minutes, depending on the size of alloy used and the mass of steel treated. Then the steel is teemed as usual into molds where no further additions should be made. The amount of alloy recommended for use in rail steel is 13 lbs. per ton, which means an addition of 0.1 per cent of metallic titanium. A higher grade alloy is not used because its rate of solution in the melted steel is slower. The price of rails treated in this way is increased about 5 per cent. For castings and soft steels a smaller amount of alloy may be added. Low-carbon steels always contain blowholes even if treated with titanium, but the steel being normally cleansed by the titanic oxide, they are free from slag and are closed up when the ingots are worked. If they become oxidized, however, or contain slag, they will open up as seams or remain as slag inclusions in the metal. It is well known that if steel is completely deoxidized and no blowholes are formed, a large shrinkage cavity, or "pipe," will form in the center of the upper part of the ingot. Titanium may cause piping, as well as other deoxidizers, but by properly designing the molds piping may be controlled so as not to give much trouble.

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*From Journal Society of Chemical Industry.

The dependence of segregation on deoxidation is less obvious than that of soundness. Primarily, segregation is due to selective freezing. The freezing-point diagram of the iron carbon alloys shows that with ordinary steel the first metal to freeze is of lower carbon content than the remaining liquid, and the last liquid to freeze is of higher carbon content than the already frozen solid. But with well-deoxidized steel this selective freezing takes place in a quiet mass of pasty material, and the higher-carbon liquid is so intricately entangled in the lower-carbon solid that it does not have chance to gather in the center of the ingot to any great extent, and is finally frozen together with the lower-carbon material. If this steel is not well deoxidized, but gives off gas during solidification the gas rises and opens up passages through the steel, taking with it a little of the higher-carbon liquid towards the top and center of the ingot and leaving the solid lower-carbon material behind. This action will result in the formation of a large body of higher-carbon material in the upper part of the ingot, or, in other words, there will be excessive segregation. Phosphorus is subject to this action in the same way as carbon, and sulphur, existing in the steel as small non-metallic globules composed of a mixture of iron and manganese sulphides with a freezing point not much, if any, higher than that of the metal, is even more effected. For this explanation of the relation between segregation and oxides in steel the writer is indebted to Mr. N. Petinot, metallurgist of the Titanium Alloy Manufacturing Co.

Aluminum and probably also vanadium and silicon have an effect on segregation similar to that of titanium, but with vanadium the cost would be higher, and with silicon and aluminum impurities would be added to the steel. In most rail steel that has been properly treated with titanium, very small angular pink inclusions can be found with the microscope. These are titanium nitride, possibly contaminated with carbide. An average of many nitrogen determinations on titanium-treated rails shows a distinctly lower amount present in solution in the metal than in untreated rails. If it is assumed that nitrogen has an injurious effect on steel, the lower amount must be an advantage for even if the whole amount removed from the metal itself is still present in the pink inclusions, it could have no more ill effects in this form than any other non-metallic inclusions of the same size. As the titanium nitride inclusions are never found segregated in groups or streaks, like alumina and silicates, but are always very small and thinly scattered, their weakening effect on the metal is practically negligible. They have been found in titanium-treated steel axles as well as rails, but not in steel castings or soft steels where smaller amounts of titanium have been used.

Some so-called "titanium-treated" steels have not been any better in regard to segregation than the average untreated steel. These have constituted, however, an insignificant percentage of the total number examined in these laboratories. In every case these segregated "treated" rails have not shown a titanium content of over 0—005 per cent (while the average treated rails are well above that figure), and the pink nitride inclusions have also been absent. These facts indicate that not enough titanium was added to produce the usual effects. In the case of deoxidation of steel with titanium an excess of probably at least 0—005 per cent is necessary.

Forty-two samples of plain and treated open-hearth steel rails have been exhaustively tested, physically and chemically, in these laboratories.

The samples have all been taken from the "A rails" or first rails rolled from the ingots, after the usual discards from their tops, thus representing in each case metal from the top part of an ingot, which would show the greatest amount of segregation and impurities. The samples were always taken in pairs, one treated and one untreated from each rolling, so that in the final comparison the influence of the conditions of manufacture could be as far as possible eliminated. The final averages of the results are here tabulated.

Chemical analyses were made at four places on each rail—at top of head, center of head, web, and flange. The lowest and highest figures for each rail were averaged together, giving the average low and high results:

	Untreated rail.		Treated rail.	
	Low.	High.	Low.	High.
Carbon	0.58	0.82	0.63	0.76
Manganese	0.71	0.78	0.75	0.79
Phosphorus	0.016	0.026	0.018	0.023
Sulphur	0.032	0.058	0.031	0.040
Silicon	0.117	0.131	0.090	0.099

The following figures relate to tests on the head of the rails:

	Untreated rails.	Treated rails.
Elastic limit	56,071	59,738
Ultimate strength	118,138	124,857
Elongation	12.8%	13.1%
Reduction of area	11.3%	15.4%
Brinell hardness	220	226
Impact resistance (Fremont machine)	1.47	1.58
Endurance (A)	1,312	1,280
Endurance (B)	16,550,920	23,923,628

(A) By Landgraf-Truner machine. Alternate bendings endured before fracture.

(B) By White-Souther machine. Revolutions before fracture.

The improvements in other rails, from lower positions in the ingot, would be much less marked, but the rails that give most of the trouble in service are the segregated "A" rails, and these are rendered practically uniform and homogeneous as the other rails by treatment with titanium. Titanium-treated rails are not better, probably, than the best possible untreated rail; but by this treatment the general standard of quality is unquestionably raised, uniformity is more nearly attained, and the bad heats of dangerously segregated or dirty steel are avoided.

To acquire still more positive data on the effect of titanium on segregation in rails, 79 "A" rails from different untreated heats and 31 similar rails from different treated heats were examined recently by means of sulphur prints and chemical analyses for carbon made on each at an upper corner of the head and at the junction of head and web. The average difference between these two points was 17 per cent for the untreated rails, and the worst rail showed 40, while only 29 of these 79 rails showed less than 12 per cent. For the treated rails the average difference was 3.1 per cent, and the worst one gave 11.5 per cent, none of the 31 showing over this amount.

The railroads have been acquiring data for some time in regard to the wear of titanium-treated rails in track, as compared with that of ordinary open-hearth rails. The results have been uniformly favorable to the treated rails, in some cases very decidedly so. For instance, on a sharp curve on the Boston Elevated Railway, titanium-treated rails laid alternately with plain rails of practically the same composition showed 41 per cent less wear after 214 days' service. In a test made by the Rock Island Railroad, titanium-treated rails in 17 months had 0.014 sq. in. abraded from their sections, on the average, while electric steel rails showed under the same conditions a loss of 0.058 sq. in., and ordinary rails 0.075 sq. in.

In axle steel it has been found similarly advantageous to use titanium for purifying the metal and preventing segregation. In steel castings the use of titanium as a deoxidizer has usually been successful and satisfactory, and in soft steel for plates and thin sheets much titanium is used. This element is preferred to any other deoxidizers because it does not leave any product of its oxidation in the steel as aluminum and silicon do, and the ingots therefore roll out smoother and the finished sheets have a better surface. Small defects on the surface of a sheet are very serious in galvanizing, so that the smoother surface of titanium-treated sheets, due to cleaner ingots, is much appreciated.

Canada's total mineral production for the calendar year 1914, according to a report issued by the Canadian Department of Mines, amounted to a total value of $128,475,499, as compared with $145,634,812 in 1913, a decrease of 11.8 per cent.

INSPECTING FOUNDRY PRODUCT.*

It is strange the way in which some manufacturers look upon inspection. A crane manufacturer told me some time ago that he didn't see the need of any inspection on his cranes. He purchased the beams of a certain mill, where they knew how to make beams; his castings came from a certain foundry, where they knew how to make castings; he had been in the business for just so many years, and he knew how to make cranes. This man was using an 8-ton hook that he arbitrarily rated up to 10 tons, and assured the purchaser that it was good for 12 tons. Another manufacturer of hooks rated it at 6 tons. Fortunately other parts of his crane were not on this free basis.

The inspector has the right to go back of the finished product and to look into the processes of production. To say that it is unjust or unfair to prescribe the manner in which a thing should be made and at the same time to define its qualities is only defensibe when the manufacturer can show that the prescribed manner of production is not the best or not a good one to produce those qualities in the product. A good inspector will satisfy himself as to the methods of manufacture as well as the evident qualities in the manufactured article.

In cast iron, test pieces, when required, are cast in sand molds, at the same time at which the castings are poured. The inspector, on his part, should see that this is the case, and the manufacturer should allow him facilities for so doing. Formerly a 1-in. square bar about 5 ft. long was used in this test. The advantage of this bar is that it can be tested in cross bending without a special machine, as the load to be hung at the middle point is only about 500 lb. Sometimes a 1-in. bar a little over 1 ft. long is used. This requires a machine, as also does the so-called arbitration bar. The latter is a round bar 1¼ in. in diameter and 15 in. long.

Manufacturers should be careful to have test bars cast the exact dimensions called for. Otherwise, an error is apt to be made in converting the results of tests to agree with specifications. It is easy to cast a bar 1⅛ in. square, when the specifications say that the bar is to be 1 in. square. It might look like giving more than is asked. Or it may be considered by some as of small importance—only ⅛ in. Again, the significance of this ⅛ in. may not be understood by the inspector, as not all inspectors are familiar with the theory of flexure. An eighth of an inch increase in the side of a 1-in. bar increases its area 27 per cent; but it increases the resistance to bending 42 per cent.

Test pieces ought to be cast in duplicate or long enough to make two breaks, so that if a flaw exists in the first break, a second can be made. Cast iron is not weakened by bending tests as tough metals would be, so that the second test, even if it be partly lapping the first, would still be a fair test.

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*Abstract by The Iron Age of a paper read April 19 by Edward Godfrey, of R. W. Hunt & Co., inspection engineers, Pittsburgh, before the Pittsburgh Foundrymen's Association.

Cast steel test specimens are cast in the shape of a coupon on the casting itself, and after annealing this is cut off and trimmed up for a tensile test. Sometimes also a bending test is required. It is important that the inspector see this coupon before it is cut off the casting and also that the coupon be left on the casting until after the annealing, so that its treatment will be the same as that of the casting.

Some trouble is occasioned on account of indefinite specifications for steel castings. Ofter a lower limit is given for the ultimate strength, but no upper limit is mentioned. At other times it is merely stated that the steel shall be of an ultimate strength, of say 70,000 lb. per square inch, and manufacturers are apt to take the stand that this is meant to be the average ultimate and to assume an allowed variation of 5,000 lb. per square inch each way. It would be well if manufacturers would ascertain from purchasers just what is wanted.

In the matter of the dimensions of iron and steel castings, the inspector is apt to meet with many variations from the ideal and correct, some of which are serious, and some are not. The most serious faults in dimensions arise from bends, warps, twists, etc., as these are generally accompanied by damaging internal strains and are due to improper treatment. Sometimes steel castings will show almost unavoidable warps or curves due to unequal cooling. The discovery of these irregularities by the inspector may lead to a means of avoiding or remedying them in later work. By weighting steel castings in the annealing furnace warps or twists may possibly be corrected. It is perhaps better to make the pattern thicker and trim off the extra metal.

Cored holes where drilled holes are called for give rise to a provoking situation. It does not meet the case to ream or drill the holes that are already cored for they cannot then be accurately located, and the holes will not be true. Castings that are to be planed and in which too scant allowance has been made in the pattern give the inspector cause for worry. Drilled holes and the planing off of the surface of a casting give the inspector an opportunity to dectect porosity or sponginess in castings that he would not otherwise discover.

Out and out rejection of what the manufacturer considers trivial leads to friction between manufacturer and inspector. An inspector is expected to exercise discretion, and the inspector who adheres too rigidly to the letter of the specifications may be doing the manufacturer an injustice. On the other hand, the manufacturer who attempts to bullyrag an inspector into accepting something questionable on the plea that he is too rigid is very frequently the one whose work will not stand much inspection. For the production of best results the inspector and the manufacturer work together. It is not always the best sign when they play together.

Whenever there is surface indication of unsoundness in steel castings, they should be regarded with the greatest suspicion. Recently an inspector objected to a steel casting of a pinion because of a small hole which he suspected was but the opening to a cavity inside. The maker of the casting pooh-poohed the idea and produced a nail with which he probed the hole and found that it did not appear to be deep. The inspector called for a bucket of water and proceeded to ascertain the size of the cavity by filling it with water. A good sized bucket of water was required to fill the hole. The effect of a cavity of this sort at the root of gear teeth can readily be understood.

When the sink-head is cut off, and there is found to be sponginess where it joins the main casting, it is an indication that its size was not great enough for the purpose. Some recommend 30 to 50 per cent.

MANGANESE STEEL.*

By JOHN H. HALL.

Manganese steel was discovered in the early eighties and was originally made by mixing molten ferromanganese and carbonless Bessemer blown metal in such amounts as to give various proportions of manganese in the finished product; consequently the ratio of manganese to carbon was practically fixed. With less than a certain amount of manganese the metal proved to be extremely brittle, and in practice the manganese was seldom less than 9 per cent, the steel generally containing 10 to 14 per cent of manganese and 1 to 1.5 per cent of carbon. The silicon is generally from 0.2 to 0.5 per cent, the sulphur is always very low, about 0.001 per cent, and the phosphorus averages from 0.08 to 0.1 per cent. Small variations in the silicon and phosphorus have little effect on the properties of the steel. The sulphur is invariably low, because the manganese of the steel eliminates it by flotation as MnS. By heating this steel to between 1,000° and 1,100° C. it can be made, if not of too heavy a section, to consist entirely of austenite.

More recent researches, in some of which the author has participated, have shown that if the carbon content of the metal is maintained at about 1 per cent, the steel will be austenite after quenching, even if the manganese content is as low as 5 per cent or even a little less; the range of carbon content within which pure austenite can be obtained is narrow with low manganese content and widens as the manganese increases. This can be more readily understood by reference to the accompanying diagram, showing part of the manganese steel series, in which the carbon content is plotted as ordinate and the manganese content as abscissa. Within the area WXYZ the steel consists of pure austenite when quenched. Steels immediately to the left of the line $C\ 1.075 - 0.04\,\text{Mn}$ are more or less martensitic when quenched; those immediately to the right of the line $C\ 1.075 + \frac{0.1\,\text{Mn}}{3}$ contain free cementite when quenched, the amount of cementite increasing as the carbon content rises. This is true also of the prolongation of the lines for a certain distance. These lines were plotted as the result of a careful research, having for its object the determination of the useful range of manganese content in these steels. The line AB represents roughly the contents of carbon and of manganese of the steels forming the basis of the original discovery and patent. The reason why the steel was found to be martensitic and brittle when the manganese was still comparatively high is apparent at a glance. The well-known diagram of Guillet, showing the micro-structure of the steels of the non-carbon manganese series, is not parallel to this diagram, as Guillet's figure represents the steel in the normalized condition; whereas in this figure the structures are that of the steel in the quenched state.

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*From Journal Society of Chemical Industry.

Properties of the Steel.—Manganese steel has a very low conductivity for both heat and electric current, a low melting point (about 1360° C.), a very high coefficient of expansion (making necessary a shrinkage allowance of 5/16 in. to the foot in foundry work), and is practically non-magnetic in all ordinary conditions. When cast it is very brittle. The cast material after heating to about 1080° C. and quenching has only a moderately high tensile strength, about 60,000 to 80,000 lbs. per sq. inch, a rather low elastic limit in both tension and compression, and a rather high ductility; its shearing strength is remarkably high. When rolled or forged and treated, the tensile strength is increased very greatly, sometimes reaching 150,000 lbs. per sq. inch, and the ductility much improved; the other properties are not much altered. The rolled material, if untreated, is quite brittle.

The chief characteristic, to which the metal owes its usefulness, is its hardness. In the treated state in which the steel has to be used, this hardness is of a peculiar kind, since, owing to its low elastic limit, the metal can be made to pean or flow when cold under the blows of a hammer to a considerable extent. In a way, therefore, the steel is soft; and hardness tests, which depend upon indenting the material, do not give high figures. Unless specially heat-treated, however, it cannot be cut with tools to a sufficient extent to make machining practicable, and its resistance to most kinds of wear is extraordinary.

As the manganese content is reduced, if the carbon be kept at the proper figure, the properties change much less than was ordinarily supposed. The strength falls off a little, the toughness diminishes progressively, and the magnetism increases a little. The resistance to wear is very little altered as long as the manganese is kept above about 5 or 6 per cent, and the tendency to pean or flow decreases as the manganese content diminishes. The usefulness of these low manganese steels is, however, rather limited by their comparative lack of toughness; they are not very brittle, like the martensitic steels of the same manganese content, but they are not nearly so tough as the steels containing over 10 per cent of manganese.

Uses.—Manganese steel is very widely used for the wearing parts of stone crushers and rolls working on hard rock, for the lips and teeth of steam shovels and ladder dredges handling rock or gravel, for centrifugal pump cases and flyers, handling gritty water, for stone screens, coal cracking rolls, drive chains exposed to grit, and other service of a similar nature. For railroad and trolley frogs, switch points, crossings, etc., the cast material is very widely used, and for rails laid on sharp curves manganese steel is almost indispensable. These rails were formerly all of cast material, but are now very generally rolled from ingots. Its tendency to flow or pean under heavy loads prevented its being used for railway car wheels. Under light loads in mine and quarry cars, blast furnace charging barrows, etc., it is widely used. The tendency to flow or pean has limited the usefulness of the metal also for types in such grinding mills as the Fuller and Griffin, and for the lining plates of the various forms of ball mills. It has long been widely used for lining plates in ball mills used in the manufacture of cement, but in many other cases it has proved to pean too much to make its use possible. In some cases, as for instance for certain sorts of grinding mill types, the use of a steel of lower manganese content, which peans less, overcomes the difficulty; the general application of these low mangaese steels to this field is, however, prevented by their lack of toughness.

Manufacture of the Steel.—The simplest and cheapest way to produce manganese steel is to mix together molten 80 per cent ferromanganese and molten soft steel containing from 0.10 to 0.25 per cent of carbon. The carbon content of the ferromanganese is such that the steel produced is of the correct composition for most purposes. The steel is seldom made by the crucible process, on account of the cost and of the difficulty of obtaining low-carbon steel by that method.

The open-hearth furnace can be used to produce the soft steel required, but the small Bessemer converter has many advantages and is more widely used. It makes cheap metal, though not quite as cheap as the basic open-hearth furnace; it provides small lots of metal distributed over the day; it does not have to be run double turn, and the cost of shutting the plant down for several days in the week is not nearly so high as with the open-hearth furnace. The Bessemer metal is not as good as open-hearth, because it is more highly oxidized, but the enormous addition of manganese will deoxidize it almost completely, and most manganese steel castings do not require better metal than can be made in the Bessemer converter.

The scrap produced, which amounts in most small foundries to 40 or 50 per cent of the fluid metal, must for complete economy be remelted. This can be done in the open-hearth furnace, although if but a single furnace is available, and the chief product is manganese steel, metal containing a great deal of manganese produces a slag which cuts into the bottom of the furnace severely. In the small bottom-blown Bessemer vessel, most of the scrap produced can be used by melting it with the pig iron in the cupola. The resulting high-manganese metal can be successfully blown by taking proper precautions, the practice being similar to that in the Swedish Bessemer shops, where pig iron containing a high proportion of manganese is frequently blown. In the side-blown converter it has so far been practically impossible to blow these high-manganese mixtures. Within the last year or two the author has conducted some experiments bearing on this problem with some success, and he hopes and expects that the problem will be solved satisfactorily within the next few years.

If the scrap is remelted in the open-hearth furnace, or remelted in the cupola and blown in the Bessemer converter, all the manganese is oxidized and lost in the slag. The yearly loss represented by this oxidized manganese amounts to a considerable sum. The most obvious solution of this problem is to melt the scrap in the electric furnace, which can be done almost without loss of manganese. In practice, however, the saving, as compared with remelting and blowing, is not very great, especially in shops already provided with a Bessemer equipment sufficient for their needs, because if an electric furnace is added to remelt the scrap, the output of the Bessemer equipment is cut down, and hence the cost of the steel made in it is raised. For this reason the electric furnace has not so far proved so useful in the manganese steel manufacture as its inventors hoped. To make electric steel cheaply, moreover, it is necessary to use a furnace of considerable size and to keep it running continuously. This is a condition not well suited to the average manufacturer of manganese steel castings.

Melting the Ferro-manganese.—As the total weight of ferro-manganese needed for the production of manganese steel is roughly one-fifth of the weight of the blown metal, it is essential that the ferro-manganese be melted. For many years crucibles have been used for the purpose, in spite of the fact that this method is more expensive than any other. The great advantage of crucible melting is that the melting losses are relatively slight.

Efforts have been made with more or less success to melt ferro-manganese in the cupola furnace. The use of this very cheap melting method has, however, not become general, because the melting losses are very high even when special precautions are taken, and these precautions necessarily complicate the operation of the cupola. The air furnace and even the small open-hearth furnace have been used to a certain extent for melting ferro-manganese, but have not been generally adopted because the melting losses are high, and, in the case of the open-hearth furnace, because night work is not commonly desirable.

The electric furnace has often been suggested as the best method of melting ferro-manganese, and is being used to an increasing extent in foreign steel works making ordinary steels. It has certain disadvantages for the maker of manganese steel in large quantities. The first is that the total melting capacity of the furnace must be high, and this necessitates the installation of one or two large furnaces. The first cost of the furnaces is high, and to keep them idle at night involves a very considerable loss. The second disadvantage is that a large bath of metal has to be melted down and drawn off a little at a time since the furnace will not melt the metal as fast as it is needed; hence a considerable expense has to be incurred for current. In many cases, therefore, it does not pay to install an electric furnace for melting ferro-manganese, unless it is used at night for melting manganese steel scrap, this necessitates pouring at night, which does not suit the ordinary small foundry; and in some cases the electric furnace will be found profitable in an existing shop only when the existing melting capacity must be increased, as it would not pay to use it if the output of the original equipment was correspondingly reduced.

Moulding Methods.—The differences between manganese steel foundry practice and ordinary steel practice are due to the greater shrinkage of manganese steel and its low melting point and great fluidity. The latter properties enable the maker to obtain sound castings in many cases with less waste of metal in sink-heads than would be possible with ordinary steel. Chills are very extensively used to assist the action of the sink-heads, and the heads themselves are often almost completely drained, leaving a mere shell of metal. The great shrinkage and the brittleness of the steel in the cast condition greatly increase the tendency of the castings to crack in cooling in the moulds. The moulds and cores often have to be broken up while the casting is still hot, and the castings often have to be cooled slowly, either by burying them in sand or by placing them when hot in a hot furnace, where they are allowed to cool slowly and evenly. Many of the castings also have to be freed from sand and placed in the treating furnace whilst still hot, to prevent cracking. The great tendency to crack also necessitates the utmost care in the design of the casting to avoid great variations in section between different parts.

Heat Treatment.—Manganese steel is heat-treated by heating it to between 1,000° and 1,100° C. and cooling rapidly in cold water. Naturally this very drastic treatment frequently results in the cracking of the casting, so that unevenness of section must be avoided as far as possible. Moreover, the low heat conductivity of the metal and its high coefficient of expansion make the heating of the castings in the treating furnace a delicate matter. If they are heated too rapidly, the outside of the heavy portions and the whole of the lighter parts outstrip the interior of the heavy sections very greatly, much more so than in the case of ordinary steel. The great expansion of the steel gives rise under these conditions to very heavy stresses, and as the steel in the cast condition is extremely brittle, these stresses are almost certain to result in the cracking of the casting. Hence heavy and complicated castings of this steel have to be heated up extremely slowly.

Rolling and Forging.—For many years the problem of the rolling and forging of manganese steel was only partly solved, and many rolled shapes were made, not from an ingot, but from a cast blank which approximated the shape of the finished product. Today, however, large ingots are successfully rolled into rails and other shapes. It is generally essential that the ingot be rolled or hammered at first very lightly all over and returned to the heating furnace before much reduction of size is attempted. The ingots are successfully brought to rolling temperatures which it was formerly thought could not be attained without risk of the ingots crumpling under the hammer or in the mill. The range of temperature within which the steel may be readily rolled is not very wide, since if it is heated too highly it will crumple, and if it is too cool it will burst the housings of the rolling mill. The heat treatment of the rolled steel is the same as that of the cast material. Frequently, however, the shape is finished slightly above the proper temperature for quenching, and is introduced into the tanks of water without reheating. Very even sections, whether cast or rolled, can be made quite tough by cooling in the air, since the toughness is roughly a function of the rate of cooling.

Metallography.—In the cast condition manganese steel consists of a ground-mass of austenite, containing manganiferous cementite in a net-work, and many needles and small lakes with the austenite grains. These cementite lakes and net-works are bounded by a zone in which the austenite is more or less transformed to troostite or sorbite. There are also places where the cementite and partly transformed austenite form eutectic. The higher the carbon the greater the quantity of this eutectic.

On heating to the treatment temperatures, the cementite is absorbed in the austenite, and is not liberated on cooling if the cooling be sufficiently rapid. In a thin bar cooled in the air there will be but little cementite liberated. In a heavy section there will be a considerable formation of cementite in the interior even after quenching, because the interior cools too slowly to restrain the separation of cementite. Hence heavy sections cannot be made as tough as light sections, and there is a distinct limit to the thickness of manganese steel castings which it is practicable to manufacture.

If the steel is cooled slowly from the treatment temperature, the cementite is liberated in a structure more or less resembling that of the cast material. The temperature at which cementite begins to be liberated, however, is several hundred degrees lower than that at which the last traces of it are absorbed in heating. Hence the castings may be allowed to cool considerably in the furnace, or in the air on the way to the tank, and yet will be quite tough after quenching; but if they are very heavy, more cementite will be liberated in their interior portions than if they had struck the water at the maximum temperature. Hence the larger the casting the more care must be taken to prevent its cooling off before quenching.

If the quenched steel be reheated to a comparatively low temperature, its toughness is almost completely removed. This is largely due to the liberation of cementite from the austenite at about 500° C., in a very fine net-work, and in countless little needles distributed broadcast through the austenite. These needles break up the continuity of the austenite, which is no doubt also partially transformed, so that the steel becomes very brittle. This brittleness, in fact, is greater than that due to cooling in the air from the treatment temperature, so that if a bar of the toughened steel be reheated at one end to a white heat and cooled in the air, it will generally break when struck with a hammer at the point where it was at or slightly below red heat. The maker of manganese steel is much troubled by claims for castings which have broken when the users heated the metal in order to bend or work it. Frequently the castings break quite a distance from the spot where it was heated, and it is then difficult to convince the customer that it was the heating which caused the damage, but microscopical examination will prove the case beyond doubt.

If heated for 24 hours or more to 500° to 600° C. the steel becomes very brittle, strongly magnetic, and very much softer as tested by the drill than in the cast or treated condition, although its Brinell hardness figure is raised. This treatment results in the transformation of the austenite to sorbite, and if the heating were sufficiently prolonged transformation to pearlite would do doubt occur. If the steel is immersed in liquid air, its magnetism is increased. On reheating this magnetic material, a critical point is found at about 730° C., accompanied by loss of magnetism. If reheated to the quenching temperature and quenched the metal is austenite and tough, but if cooled slowly it will be brittle and will show the same micro-structures as if it had never been made magnetic.

The controversy which is now raging as to the existence of B-iron has involved manganese steel, and much new data has been published on the behavior of manganese steel in heat treatment. It has long been claimed by some that there are features in the behavior of manganese steel which the allotropic theory will not explain. I personally have not yet found a treatment of the metallography of manganese steel which the allotropic theory fails to explain. In fact, when I first investigated the metallography of manganese steel I was able to save myself a great deal of labor by using the carbon-iron diagram and the allotropic theory as a guide.

GOLD-PLATINUM-PALLADIUM DEPOSIT IN SOUTHERN NEVADA.

Platinum and its closely allied metals palladium, iridium, and others are among the few mineral products for which the United States is dependent on foreign countries. Platinum is indispensable to the chemist and in recent years it has also come into vogue in the manufacture of jewelry. It is extensively used for chains and for the setting of diamonds, the claim being made that the platinum, besides being more resistant than silver and harder than gold, sets off the diamonds more effectively. Palladium resembles platinum but has a higher luster, like that of silver, and is used as an alloy with platinum to give this metal increased brilliance and for other technical purposes. The demand for palladium is considerably greater than the supply, and in the last few years the price of platinum and palladium has been double that of gold.

It is therefore of interest to learn that platinum and palladium have been found in ores of the Yellow Pine mining district, in Clark County, Nevada. The principal find was made at the Boss mine, which is described in Bulletin 620-A, recently issued by the United States Geological Survey. The ore deposit on the Boss claim was discovered some 30 years ago, having been located for copper, the presence of which is plainly indicated by chrysocolla and other oxidized copper minerals. In the nineties a leaching plant was built at Goodsprings, 12 miles from the mine, and an attempt was made to treat the oxidized copper ore, but the process proved a failure. Not until recently was the gold and platinum content of the ore recognized. The failure to recognize, or at least fully to appreciate, the gold-bearing character of the ore seems to have been due to the fact that much of the gold is very finely divided and cannot be obtained by panning, and also to the fact that some of the extraordinarily rich material when panned yields a black residue that might easily be and probably was thrown away as worthless black sand. Systematic sampling of the deposit early in 1914 led to full recognition that gold is present in valuable amount, and it was during the course of this sampling that the platinum and palladium content of the ore was discovered.

The deposit consists of a mass of fine-grained quartz inclosed in dolomites of Carboniferous age. The precious metals are especially associated with a rare mineral that is known by the rather unwieldy name plumbojarosite; it is a hydrous sulphate of iron and lead. The mineral is locally known as greenish talc, and this name accurateuly describes its main physical properties; pockets of the pure mineral carry 100 ounces or more of platinum and palladium and several hundred ounces of gold to the ton. This exceeding richness points to a concentration of the precious metals in the oxidized ore by surface solutions, so that in depth the pockets of extremely high grade ore, such as are now being extracted, will give place to ore of moderate grade.

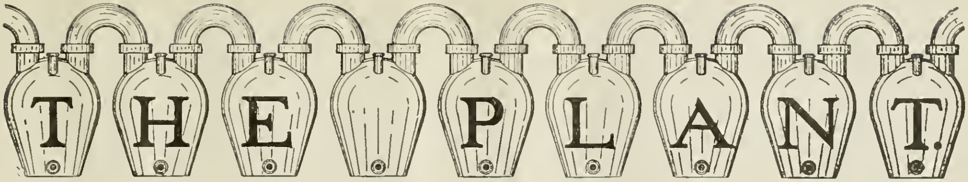
MELTING POINT OF COPPER ALLOYS.

The results of tests of a few typical alloys made by H. W. Gillett and A. B. Norton of the United States Bureau of Mines are summarized as follows:

	Approximate Composition				Melting Point	
Alloy.	Copper.	Zinc.	Tin.	Lead.	°Cent.	°Fahr.
Gun metal	88	2	10	..	995	1825
Leaded gun metal	85½	2	9½	3	980	1795
Red brass	85	5	5	5	970	1780
Low-grade red brass	82	10	3	5	980	1795
Leaded bronze ..	80	..	10	10	945	1735
Bronze with zinc	85	5	10	..	980	1795
Half-yellow-half-red	75	20	2	3	920	1690
Cast yellow brass	67	31	..	2	895	1645
Naval brass ...	61½	37	1½	..	855	1570
Manganese bronze	..	..	..	..	870	1600

The melting point given is the "liquidus," or point where the alloy is completely molten. The temperatures are thought to be accurate within plus or minus 10° C. or plus or minus 20° F.

New regulations governing the use of coloring matter in foods have been promulgated under the Canada Adulteration Act by an order of Jan. 9, 1915. It is provided that the following articles may be artificially colored, if only harmless coloring matter is used, without a declaration to that effect on the label or elsewhere, although such coloring substance shall in no case be employed to conceal damage or to appear to enhance the value of the product: Full whole-milk cheese; confectionery, including jelly powders; flavoring extract of lemon; ice cream and ices; butter. In the case of spirits, vinegar, sauces, fermented beverages not subject to excise requirements, and so-called "temperance" beverages, the use of caramel only is permitted without declaration of such coloring. The use of artificial coloring must be stated on the label in easily legible type in the case of all other food products. The following substances are provisionally considered to fall within the definition of harmless coloring materials: Caramel; cochineal; saffron, chlorophyll and innocuous vegetable color extractives; certain coal-tar dyes not containing arsenic in excess of 10 parts As_2O_3 per million, calculated on the actual weight of coloring matter, and not containing heavy metals (except iron), when used in quantities not exceeding 2 grains per pound (1 part in 3,500). The use of copper salts in the greening of peas is permitted, provided the amount of copper (expressed as metallic copper) in the peas does not exceed 80 parts (by weight) per million in the drained peas or 10 parts per million in the liquid.



FIXATION OF ATMOSPHERIC NITROGEN.*

By LELAND L. SUMMERS.

INTRODUCTORY.

In 1898 Sir William Crookes in his address as President of the British Association very forcibly pointed out that the commercial fixation of atmospheric nitrogen was one of the greatest discoveries awaiting the ingenuity of chemists. He emphasized with very interesting figures its important practical bearing on the future welfare and happiness of the civilized races. This address brought forcibly to the attention of engineers the fact that the existing sources of fixed nitrogen were limited, and greatly stimulated the efforts of investigators. The problem itself had been worked on for over a century, as it was known that nature fixed nitrogen of the atmosphere by means of electric discharges, and Cavendish in 1781 had shown that a small amount of nitrogen was converted into nitric acid in the combustion of hydrogen with oxygen to form water, while Bunsen in 1877 obtained favorable yields by means of gaseous explosions. The earlier efforts commercially in the art were, however, largely confined to the fixation of nitrogen for the purpose of manufacturing cyanides, and the earlier bibliography of the subject therefore deals almost entirely with these efforts.

Commercial Products of Nitrogen.—The three fundamental commercial products formed by nitrogen are: first, its union with oxygen to form nitrates, XNO_3, and nitrates, XNO_2; second, its union with carbon to form cyanogen C_2N_2 and producing cyanides XCN and cyanamids XCN_2; third, its union with hydrogen to form ammonia, NH_3. From all of the above products there are obtained a large number of derivatives used the chemical arts.

The most important of all commercial products are the unions of nitrogen with oxygen, forming the nitric acid salts of commerce. These are of particular importance on account of the vast natural deposits of nitrate of sodium occurring in Peru and Chile, commonly called Chile saltpeter. Practically, this commodity is the one that sets the price for all other compounds of nitrogen, as it has been mined in Chile since 1830, and during the past twenty-five years its production has assumed vast proportions, the present annual output amounting to about 2,500,000 tons. This deposit of Chile appeared inexhaustible, and therefore there was no occasion for alarm regarding the world's supply of combined nitrogen; but after years spent in exploration work it began to appear that the Chilean deposits would be exhausted before the end of the present century, and since then all other sources of combined nitrogen have received attention.

While there are a few scattered natural deposits other than those in Chile, there is none which has at the present time a chance of competing, most of them being of limited extent and situated in inaccessible regions. In Chile the deposits are easly worked, and even after years of careless mining, with no effort to effect economies, the present cost of producing nitrate is not excessive, varying from $10 to $20 per ton and selling in Liverpool for about $45 per ton. This leaves a profit of from $5 to $10 a ton on the operation, after paying the Government of Chile an export tax of about $12.25 per ton. In the past thirty years this export tax has netted the Chilean Government about $500,000,000. Of the total production of Chile the United States imports about 600,000 to 700,000 tons per annum, the balance being practically all shipped to European countries. Chile saltpeter has sold as high as $60 a ton, but since 1909, when the agreement among the producers expired, the price has approximated $45 per ton f. o. b. Liverpool, making a price of from $35 to $40 per ton f. o. b. Chile.

The union of nitrogen and carbon to form cyanides and with hydrogen to form ammonia are two of the earliest forms in which the combined nitrogen was utilized. Most all animal and vegetable refuse contains ammonia compounds, and these were the early sources of ammonia, and animal refuse products such as hides, hoofs and horns were the cources of combined carbon products forming the cyanides. Until the discovery of the McArthur-Forrest process for gold extraction, the markets for cyanides were comparatively limited and there was no great effort made to produce them on a large scale. With the rapid development of this art in the recovery of the low-grade gold deposits, a sudden impetus was given to the cyanide industry, and large quantities of cyanides are now manufactured from ammonia and metallic sodium. Small amounts of cyanides for industrial purposes are recovered from the gas retort houses, but these processes are not generally applied, and no particular effort has been made to extend the processes to the recovery of cyanids from by-product coke ovens. The greater portion of the cyanides are manufactured in England and Germany, and some 20,000 tons per annum are exported annually by these two countries. As the cyanides of sodium and potassium for gold recovery purposes sell from \$300 to \$400 per ton, they represent one of the highest prices of nitrogen directly combined with a simple element.

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The third great commodity of commerce, ammonia, is utilized extensively in industrial arts, but, in addition has been used for many years as a fertilizer. The annual production of sulphate of ammonia now amounts to about 1,250,000 tons, and the Liverpool price approximates that of sodium nitrate, varying from \$45 to \$60 per ton. Practically all of this sulphate of ammonia is manufactured from coal distillation either from gas-house retorts or by-product coke ovens, up to the past year there having been practically no process in operation for the direct synthesis of ammonia from its compounds.

All the older retort processes for the manufacture of gas recover ammonia by washing the illuminating gas with water. All by-product coke ovens likewise treat the by-product gas for the recovery of ammonia. American coals run from 0.9 per cent to 1.4 per cent nitrogen, or from 18 to 28 lb. (8.1 to 12.7 kg.) of nitrogen per ton of coal. In the distillation of this coal, about 20 per cent of the nitrogen is recovered from the gases of distillation, so that from 4½ to 7 lb. (2.1 to 3.2 kg.) of ammonia are recovered per ton of coal distilled; this ammonia when united with sulphuric acid forms sulphate of ammonia, giving a yield from 18 to 28 lb. (8.1 to 12.7 kg.) of sulphate of ammonia per ton of coal distilled. Weak solutions of ammonia water are concentrated from the gas-house retorts and the ammonia distilled from this water by breaking down the ammonia contents with lime, the pure ammonia being then united with sulphuric acid. In many of the coke oven plants the sulphate is formed directly by passing the gases into sulphuric acid, forming the ammonia sulphate by a direct process.

In general it costs about \$15 per ton of ammonia sulphate to manufacture the sulphate from the ammonia, so that if ammonia sulphate is selling for \$45 per ton, \$15 of this is represented in the cost of sulphuric acid and the manufacturing, making the net ammonia cost, with profit, \$30 per ton of sulphate or, as the nitrogen content of the sulphate amounts to 21 per cent, the nitrogen represents an actual value of 7 cts. per pound. With the great increase in the number of by-product coke ovens, there has been a greatly increased quantity of ammonia sulphate manufactured, and it would seem that under these conditions the price of ammonia sulphate will tend to diminish rather than to increase. The actual cost to the by-product coke oven plants recovering the ammonia, in addition to the \$15 for manufacturing the sulphate of ammonia, will approximate \$10 per ton, and if there is any profit to be obtained from the sale of ammonia, they can afford to recover it at this figure.

Another source of ammonia by coal distillation is from producer gas generated on what is known as the Mond system. In this process steam is admitted to the producer in excess, so that the temperature is not permitted to rise to a point where the ammonia liberated by the fuel is decomposed. This excess of steam tends to protect the ammonia, and it is recovered from the producer gas by washing. In this process not only the ammonia carried in the volatile products is recovered, but also a large percentage which ordinarily remains in the carbonaceous residue of the coke oven and gas-house retort. As ordinarily distilled, about 50 per cent of the total ammonia of the coal remains in the coke residue and is not recovered. In the producer, where this coke is consumed in the presence of steam, the total percentage of recovery may be as high as 75 per cent of the theoretical nitrogen contained in the coal, so that from 15 to 20 lb. (6.8 to 9.1 kg.) of nitrogen may be recovered, or, in terms of ammonia sulphate, from 60 to 80 lb. (27.2 to 36.2 kg.) of ammonia sulphate may be obtained per ton of coal consumed in the producer. This type of producer has not been extensively utilized in America, as the expense of installation is increased by the necessity of washing a very large volume of low-grade gas, the volume of gas per ton of coal consumed in the producer being about 130,000 cu. ft. against about 10,000 cu. ft. per ton of coal, as distilled in the coke oven.

A number of these plants have been installed in England and on the continent, but the aggregate of the ammonia sulphate produced is not large as compared to that from coke ovens and gas house retorts.

Available Nitrogen in Commercial Products.—The question of the available nitrogen in the various compounds has, in a measure, determined the price of the product, the utilization in the fertilizer art being practically the basis of fixing the price. For a number of years it has been assumed that the selling price of combined nitrogen would be from 12 cents to 13 cents a pound. Thus Chile saltpeter being about 95 per cent pure, nitrate of soda would have a theoretical nitrogen content of about 16.5 per cent or, corrected for impurities, would have about 15.5 per cent nitrogen.

As the cyanides, until recently, were not used directly in the fertilizer art, and were combined with more expensive products, their price has not been regulated by their content of combined nitrogen. The ammonia used in the fertilizer art is almost entirely used as sulphate of ammonia, on account of the cheapness of the commercial sulphuric acid and the ease of manufacture, and this product would therefore have a theoretical content of 21 per cent of nitrogen.

The above nitrogen products may be considered the fundamental commercial forms in which combined nitrogen enters the market, and while the fertilizer industry fixes the price of combined nitrogen, it is only one of the many industries in which vast quantities of nitrogen are utilized. Thus about 50 per cent of all the Chile saltpeter imported in this country is used in the manufacture of explosives, while an additional 25 per cent is utilized in the arts requiring nitric acid. Of the ammonia sulphate, a very large percentage is used directly as fertilizer, though there is a very considerable demand for use in chemical industries and such commercial applications as anhydrous and aqueous ammonia used in the refrigeration art. Practically all explosives have utilized nitrogen compounds as a principal ingredient. The earlier makers of black gunpowder used Chile saltpeter, charcoal and sulphur and the later so-called smokeless powder utilizes the oxygen-carrying property of nitrogen as well as the inherent molecular energy in the production of such high explosives as nitroglycerin, cordite, lydite, mellenite, gun cotton and various other nitro-cellulose compounds, and modified explosives used in industrial work, such as dynamite and various blasting powders.

Fixation Processes.—In considering the fixation of atmospheric nitrogen from a commercial standpoint, the limitations will be imposed by the selling price of the natural product from Chile, covering nitrate compounds, and the selling price of ammonia sulphate, as obtained from coal distillation, affected as these prices will be by the manufacture of ammonia from atmospheric nitrogen.

In competition with the above sources of nitrogen there has been the constant effort toward the fixation or rather the utilization of some of the vast quantity of atmospheric nitrogen surrounding us.

A list of these fixation processes would contain the names of hundreds of investigators, and from the past twenty years of effort there may develop processes which at present are still experimental; but of the various processes which have reached the state of commercial application there appear to be four distinct lines of development.

First. The production of nitric acid directly from the atmosphere by means of the electric arc. In this process the nitrogen of the atmosphere is directly combined with its accompanying oxygen without utilizing any other chemical substances, the process consisting essentially of a powerful arc furnace through which air is forced, causing at this high temperature the nitrogen to combine with the oxygen, forming nitric oxide, NO.

Second. Methods of fixing nitrogen by means of electric furnaces or combustion where the energy of chemical combination is utilized, causing the nitrogen to combine with some substance with which there is a pronounced energy of chemical combination. These processes include furnaces utilizing calcium carbide, with which nitrogen readily combines to form calcium cyanamid, $CaCN_2$, and various processes for making combinations of nitrogen and a basic or alkaline earth metal such as calcium nitride, Ca_3N_2 or magnesium nitride Mg_3N_2 or aluminum nitride AlN, the chemical action usually forming a nitride or carbonitride.

Third. Processes for producing ammonia, NH_3, directly from nitrogen and hydrogen. These include the effort to use the various forms of electric discharge by which the nitrogen molecule may be decomposed and, in the presence of hydrogen, form ammonia. As ammonia decomposes at a very low temperature (500 to 1,000° C.), only the silent discharge seems available, and the yields are not commercial. The most promising of all direct ammonia processes seems to be that of Haber. In this process a catalytic agent is used, and under a heavy pressure the nitrogen molecule is decomposed and united to the hydrogen, thus forming ammonia. Salts of uranium seem to be preferred as the catalytic agent, and have the power of acting on nitrogen at a temperature of about 500° C.

Fourth. Production of a high temperature by combustion, utilizing either catalytic agents or simply by producing a high temperature by means of the explosion or combustion of gases directly combining the nitrogen and oxygen to form nitric oxide, NO. This method, early used by Bunsen in the combustion of hydrogen to form water, has been applied to coke oven gases by Hausser. A bomb is used and the mixture of gas and air is fired electrically, the small amount of NO formed is recovered and converted into nitric acid, HNO_3.

The chemical form in which the commercial supplies of combined nitrogen appear on the market is due largely to existing commercial conditions. The nitric acid combined as sodium nitrate occurs in this form simply on account of being naturally produced in this form. The ammonia appears on the market as ammonia sulphate largely on account of the cheapness with which sulphuric acid can be obtained, and the widely distributed plants for its manufacture, making it one of the cheapest and most convenient forms of combining with ammonia. It is probable that in commercial nitrogen fixing plants, if both ammonia and nitric acid are manufactured, one of the most convenient forms of marketing this product will be by using nitric acid in place of sulphuric acid, making ammonia nitrate, NO_3NH_4. This product is on the market at present, but is only manufactured from sodium nitrate and from ammonia, or in some of the plants where nitric acid is manufactured, ammonia is shipped to the nitric acid plants to be manufactured into ammonia nitrate. The advantage of ammonia nitrate is that it has a nitrogen content of 35 per cent in this respect, being a much more concentrated nitrogen product either for the processes of manufacturing other compounds of nitrogen or for use in the fertilizer industry.

Physical Limitations and Those Fixed by Natural Sources.—The competition with natural sources will fix the commercial limitations or selling prices for these various nitrogen compounds and in considering the possible developments of the processes it will be interesting to see to what extent they have definite theoretical limitations, as these will greatly affect any comparison of possibilities. Before considering in detail these processes we might endeavor to investigate whether our present conception of the physical and chemical reactions involved impose real limitations, or whether there is an uncertain boundary which further developments may encroach upon, perhaps thus continually improving the efficiency and possibilities commercially. If, for instance, the nitric oxide processes which utilize only 2 per cent to 4 per cent of the energy supplied to the furnace are limited to this amount by the inefficiency of the apparatus, there is much greater possibilities of development than would be the case if the process has definite physical or thermodynamic limitations, and the present apparatus utilizes a favorable percentage of this possible ultimate limit. To some extent these theoretical limitations are not always sharply defined, and research will extend this horizon, but we may determine some of these limitations quite definitely.

II. THEORETICAL LIMITATIONS.

As we are considering this subject from its engineering aspects, it may be excusable to examine some of the theoretical limitations imposed by the laws of physical chemistry, and in reviewing what may be termed elementary formula, it is interesting to note that the investigation of these theoretical limitations has been of fundamental importance to physical chemistry in extending the application of the laws of chemical dynamics.

Molecular Inertness of Nitrogen.—The elements carbon, C, and nitrogen, N, possess a marked similarity in the fact that the molecule of each is composed of two or more atoms united together with a bond representing a large amount of energy. Nitrogen, having an atomic weight of 14, has a normal molecular weight of 28, indicating two atoms to the molecule, and in this molecular form it occupies 79.2 per cent of the volume of the earth's atmosphere. To separate this molecule into its constituent atoms and cause these atoms to combine with other elements is the problem of the fixation of nitrogen. Unless combined in the atomic form, the enormous bond between the atoms causes them to combine upon themselves into the inert form of molecular or atmospheric nitrogen. The ordinary compounds of nitrogen are formed only by expenditure of a large amount of energy, the union of molecular nitrogen, N_2, and molecular oxygen, O_2, to form nitric oxide, NO, being represented by the formula,

$$N_2 + O_2 = 2NO = -43{,}000 \text{ calories.}$$

Or in other words, to form one gram molecule of nitric oxide, NO, requires the expenditure of energy amounting to 21,500 calories.

The general similarity to carbon in this molecular inertness makes an interesting comparison.

Thus

$$C_2 + O_2 = 2CO = 58{,}000 \text{ calories}$$

$$2CO + O_2 = 2CO_2 = 134{,}000 \text{ calories.}$$

The formation of one gram molecule of CO therefore represents the liberation of 29,000 calories, while the formation of one gram molecule of CO_2 and CO represents 67,000 calories or a total of 96,000 calories in the formation of CO_2 from the original elements C and O. When amorphous carbon therefore is caused to assume the gaseous condition and unite with a molecule of oxygen, there is liberated 29,000 calories, but after assuming this condition in which the molecule is no longer composed of the inert carbon molecule, a second gram molecule of oxygen unites with the CO and liberates 67,000 calories additional. The second molecule of oxygen therefore liberates 38,000 calories more than the first molecule, and as the oxygen molecules were alike, this energy represents the bond uniting the carbon atoms and the energy necessary to break down the bond between these atoms and produce a gaseous condition from the amorphous condition.

Returning to the nitrogen molecule, it is apparent that the formation of the gram molecule of NO requires 21,500 calories in comparison to carbon liberating 29,000 calories to form CO; that is, the nitric oxide reaction is endothermic while the carbon monoxide reaction is exothermic. Upon adding a second molecule of oxygen to the nitric oxide to form the peroxide, we find,

$$2NO + O_2 = 2NO_2 = 27{,}000 \text{ calories}$$

or 13,500 calories per gram molecule are liberated after previously expending 21,500 calories to form NO. Since there is liberated only 13,500 calories upon adding a second molecule of oxygen, the net energy required to form NO_2 would be 8,000 calories. The first molecule of oxygen required 21,500 calories, whereas the second required only 8,000 calories, so that 13,500 calories were required by the nitrogen molecule to prepare it for combination with the oxygen.

Dynamic Equilibrium.—These heats of combination developed by the atoms combining upon themselves indicate a very stable or inert molecule, and in liberating this energy to assume this more stable form, the forces exerted are of large magnitude. It is readily apparent from this, for instance, how carbonaceous gases can readily form soot and cinders and other amorphous forms, when the union with oxygen is disturbed as the tendency of the atoms to unite with oxygen or to form carbon molecules will depend upon an adjustment of the surrounding conditions. This ever-changing condition of equilibrium constitutes the dynamic conception of equilibrium displacing the static equilibrium of the older theories of chemistry. In order to more carefully consider some of the theories that have been advanced, it may be of interest to follow further some of the concepts of physical chemistry. The fact that the nitrogen atom has this strong tendency to combine upon itself with a liberation of energy greater than the combination with the oxygen atom, indicates that in any reaction, when the combination with oxygen has made possible a changing of the atoms, there will be continuously in progress an action and a reaction and the equilibrium will be indicated by the expression

$$N_2 + O_2 \rightleftarrows 2NO$$

the sign of equality being displaced by the two arrows indicating that the action proceeds in each direction; that is, it is a reversible reaction, and the equilibrium will be dependent upon conditions, the two most important conditions being temperature and the active masses of the substances present. Considering first the effect of the active masses present, if it be assumed that the collision of molecules causes the rearrangement of the atoms comprising the molecule, and that of these collisions only a certain number will cause the re-arrangement to proceed in one direction, the re-arrangement will be greater the more frequently the collisions take place, there being some ratio for each individual case, and the collisions possible will obviously be proportional to the concentration present; that is, the collisions will be proportional to the number of molecules present. With two substances present, the collisions will be proportional to the molecules of each present and hence to their product.

The Velocity Coefficient. If C_1 and C_2 represent the special concentration of gram molecules present, the velocity of the reaction will be proportional to C_1C_2 or the velocity V of the reaction will be

$$V = C_1\,C_2k$$

where k is a constant or coefficient to be determined for the given temperature. This velocity of reaction will proceed each way in reversible reactions, the concentrations of the molecules in the reverse action being represented by C_1' and C_2' and the velocity of reaction by V' the velocity of the reaction in the reverse direction will be

$$V' = C_1'\,C_2'k'$$

where k' is the velocity constant to be determined for the reverse reaction.

The Equilibrium Constant. The chemical driving force for any reaction will continually diminish as the reaction approaches equilibrium, or the velocity of the reaction will diminish as equilibrium is approached, and when equilibrium is reached V will equal V' and

$$kC_1\,C_2 = k'C_1'\,C_2'$$

This dynamic equilibrium indicates that as much reactive substance is being formed in a given time as is being decomposed, and a fixed relation therefore results, but the reactions have not ceased, only the velocities have equalized, and the driving chemical forces are incapable of making any further change in the reacting substances unless the velocity in one direction or the other is changed. In this state of equilibrium the ratio between the velocity coefficients or constants is

$$\frac{k_1}{k} = \frac{C_1'\,C_2'}{C_1\,C_2} = K \text{ equilibrium constant.}$$

Or, as the concentration or active mass in any reaction increases, the velocity coefficient increases, and for each change in equilibrium due to temperature change there is a definite concentration ratio represented by this equilibrium constant K.

Partial Pressures. If the concentration of a given molecule is C and the collisions of the molecule are proportional to this concentration, if there are two molecules the collisions between the two similar molecules will be C times as great as one molecule, or C^2. As the total pressure of a mixture of gases is the sum of the pressure of each gas, and by Avagadro's hypothesis the pressure is proportional to the number of molecules in the given space, the concentrations instead of being represented by gram molecules C may be expressed as partial pressure p, and equilibrium will be represented by the ratio of the partial pressures of the gases. Thus two molecules of NO will have the pressure p^2_{no} while p_n and p_o may represent the pressure of the N and O. At equilibrium the constant K will then become

$$K = \frac{p_{2no}}{p_n\ p_o}$$

and for any pressure and volume the familiar equation

$$PV = RT$$

will represent the work done. Where P is the pressure, V the volume, R the gas constant, and T the absolute temperature. The work done in the reaction

$$N_2 + O_2 = 2NO$$

will consist in taking one molecule of N from the pressure p and transferring to the pressure P also one molecule of O from the pressure p, to pressure P, and offsetting this work will be the transferring of two molecules of NO from pressure P_{no} to p_{no} when the pressure of a gas at constant volume is increased by the infinitely small amount dp, the corresponding work done dA will be

$$dA = dpV$$

The Maximum Work. If we substitute for V its value from the equation

$$pV = RT$$

we have

$$V = \frac{RT}{p}$$

and

$$dA = \frac{RTdp}{p}$$

and for the work done between the limits of pressure p and P we have

$$A = RT\int_P^p \frac{dp}{p} = R\,Tln\,\frac{p}{P}$$

where ln is the natural logarithm. For the work done in forming the NO at a temperature T, we will have

$$A = R\,Tln\,\frac{p_n}{P_n} + R\,Tln\,\frac{p_o}{P_o} - 2R\,Tln\,\frac{p_{no}}{P_{no}}$$

or simplifying and assembling the initial pressures and the final pressures in separate terms, we have for constant temperature

$$A = R\,Tln\,\frac{p_n\ p_o}{p^2_{no}} + R\,Tln\,\frac{P^2_{no}}{P_n\ P_o}$$

But the first term represents the initial pressures or the work done on the initial condition of the materials, and we are not called upon to furnish this energy, the change of energy being represented only by the second term

$$R\,Tln\,\frac{P^2_{no}}{P_n\ P_o}$$

This quantity $\frac{P^2_{no}}{P_n\ P_o}$ is, however, the ratio of pressures or concentrations represented by the equilibrium constant K and hence the work done at any given temperature may be represented by the equation

$$A = RTlnK$$

Van't Hoff has applied this type of fundamental equation to a wide range of reactions, and by means of the second law of thermodynamics has made it applicable to temperature and concentration changes in which the latent energy plays an important part, for in these reactions the product of the specific heat by the temperature no longer represents the heat transfer.

Van't Hoff's Fundamental Equation. The second law of thermodynamics expresses the relation of A, the maximum work possible at a temperature T, and U, the decrease in energy of the system in relation to the ratio of change of A with the temperature T, the equation being

$$A - U = T\,\frac{dA}{dT}$$

Substituting in this the value of A and $\frac{dA}{dT}$ obtained from the equation

$$A = RTlnK$$

we have when both A and lnK change with the temperature T

$$\frac{dA}{dT} = RLnK + RT\,\frac{dlnK}{dT}$$

and hence

$$U = -\,RT^2\,\frac{dlnK}{dT}$$

which is van't Hoff's fundamental equation for chemical reactions in which the heats of reaction U are important factors, and both the temperature and concentrations may be variable. The quantity U, which in thermodynamics represents the decrease in energy of the system, may here represent the energy of chemical combination, which changes very little with changes of temperature and is generally designated as Q, and in the case of nitric oxide it has the value 21,500 calories per gram molecule; so the equation becomes

$$43{,}000 = -\,RT^2\,\frac{dlnK}{dT}$$

and when using the air as a source of nitrogen in which the nitrogen content is 79.2 per cent and the oxygen 21.8 per cent and letting x represent the percentage of NO formed, as ½ x will be from the nitrogen and ½ x from the oxygen, the equilibrium constant K will be

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right)\left(20.8 - \frac{x}{2}\right)}$$

Nernst's Determinations of Equilibrium. Nernst and his assistants determined x for a number of temperatures, the calculated and observed values being as follows:

T	X (Obs.)	X (Calc.)	Observer.
1811	0.37	0.35	Nernst
1877	0.42	0.43	Jellinek
2023	bt. 0.52 and 0.80	0.64	Jellinek
2033	0.64	0.67	Nernst
2195	0.97	0.98	Nernst
2580	2.05	2.02	Nernst-Finckh
2675	2.23	2.35	Nernst-Finckh

Nernst's calculations of x or equilibrium volumes in per cent of NO, using air at temperatures of 1,500 deg. T to 3,200 deg. T are plotted in Fig. 1.

Rapidity of Dissociation. Nernst and Jellinek also determined the rapidity with which the NO is decomposed or dissociated at the various temperatures, and these experiments showed that the tendency of NO to revert to molecular N and O is very slight below a temperature of 1,500° C., but increases very rapidly with the temperature, so that the time of withdrawing the products through the varying zones of heat in the electric arc is sufficient to effect a large amount of dissociation. In order to avoid this dissociation a rapid movement of the air through the arc or the arc through the air is desirable, and this in turn causes increased radiation and convection losses, so the maximum possible temperature of the arc is not obtained, and hence there are imposed very distinct limitations to the yield of NO.

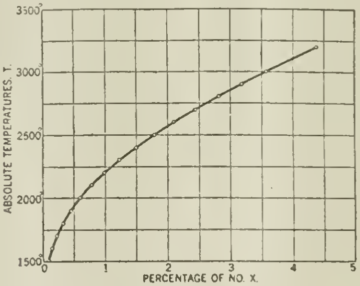

Fig. 1.

Haber's Theory of Ionic and Electronic Collisions. Haber and Koenig investigated the possibility of utilizing lower temperatures in the arc to avoid dissociation by enclosing the arc in a water-cooled quartz tube, whereby moderate temperatures were preserved. In place of the molecular collisions we have assumed above as due to the thermodynamic condition of the gas, they used a vacuum and endeavored to utilize the kinetic energy from the rapid motion of the ions and electrons liberated by the arc stream under these conditions. Haber considered it possible to increase the thermodynamic concentrations about 50 per cent. His tests indicated that using a temperature of 3,000 deg. cent. it was possible to show 10 per cent concentrations of NO, which would correspond to a temperature under the thermodynamic equilibrium of 4,300 deg. cent. Haber gives a table showing the effect of various mixtures of N and O when working with the increased mean free path of the molecules due to a vacuum of 100 mm. of mercury. In his work Haber prefers to use the square root of the equilibrium constant *K* we have used above, thus enabling the partial pressures of the resulting substances to be read direct, while the partial pressures of the ingredients are expressed as square roots of the pressures.

Haber's table for a pressure of 100 mm. is as follows:

	Gas Mixture.				Thermodynamically Calculated Absolute Temperature by	
	O_2 Percent.	N_2 Percent.	Percent NO.	$K = \frac{(NO)}{(N_2)^{1/2}(O_2)^{1/2}}$.	Haber.	Nernst.
Air	20.9	79.1	9.8	0.284	4365	4334
Half-half Mixture.....	48.9	51.1	14.4	0.337	4686	4650
	44.4	55.6	14.3	0.337	4686	4650
Reversed Air Mixture...	75.0	25.0	12.8	0.357	4805	4767
	81.7	18.3	12.1	0.397	5042	5000

The yields of NO per kilowatt hour obtained by Haber were unsatisfactory, and the complications of small water-cooled tubes and working under a vacuum of 100 mm. have not justified commercially the higher concentrations of NO he obtained.

Commercial Processes Now in Use Have Distinct Limitations. We may assume that up to the present the processes in commercial use are limited strictly by the thermodynamic equilibrium of the van't Hoff equation. As the volume of gases when working with low concentrations of NO are considerable, the radiation and convection losses as well as the transfer of sensible and latent heat from the arc to the gases lower very materially the temperature of the arcs, and the yields therefore indicate an average working temperature of 2,200 deg. cent. to 2,500 deg. cent, or concentrations of 1.5 per cent to 2 per cent NO when working with air. These theoretical limitations of the direct process of forming NO have therefore led to many efforts to dissociate the nitrogen molecule by other means.

Sources of Chemical Energy. Naturally the sources of chemical energy have offered a most fruitful field, but, like the synthesis of carbon compounds, a considerable elevation of temperature is necessary before the chemical energy becomes effective enough to break the bond of the nitrogen molecule. At these elevated temperatures practically all elements or compounds which release sufficient energy to combine with nitrogen have a greater combining power for oxygen, so the processes cannot be conducted with air, but involve the separation of the nitrogen from the oxygen of the air as a preliminary step. The compounds of nitrogen thus formed do not therefore include the oxides of nitrogen. The common elements exhibiting the most pronounced tendency to combine with nitrogen are calcium (Ca), magnesium (Mg), aluminum (Al), boron (B), etc. The carbides of a large number of metals also exhibit a pronounced tendency to combine with molecular nitrogen when heated.

The great advantage from a theoretical standpoint in utilizing these processes is that the reaction with nitrogen may be made more complete as equilibrium may be continually disturbed by withdrawing the compound of nitrogen formed or by presenting to the nitrogen to be combined fresh combining surfaces of the substance, and the action may be caused to proceed practically quantitatively, thus avoiding heating large quantities of materials which are inert to the reaction. A vast field of research is opened by these possibilities, as very few of the equilibrium figures have been determined, and it is almost certain that direct combustion methods may eventually be evolved along these lines.

The experimental data are so meager that no theoretical limitations can be placed. The reactions assume unusual importance however on account of a wide application in the arts. This may be best illustrated by considering the formation of calcium carbide, CaC_2, in relation to its three reversible reactions, namely,

$$\begin{aligned} &(1)\quad CaO + 3C \leftrightarrows CaC_2 + CO \\ &(2)\quad CaC \leftrightarrows Ca + C \\ &(3)\quad CaO + C \leftrightarrows Ca + CO \end{aligned}$$

There are here six substances, some in solid form, some in liquid and some gaseous (molecular and atomic), and it is evident that the temperature will have a marked influence on the equilibrium which will exist, and the reaction will be greatly affected by very minute changes, for the partial pressure of the gases will be suddenly changed by such conditions as the carbon released in a gaseous state immediately combining to form amorphous carbon, or the metallic calcium vapor combining with the oxygen released by the CO to form calcium oxide, which immediately precipitates as a solid. The fact that calcium oxide, which is most refractory, can be vaporized at a temperature of 1,600 deg. cent. to 1,800 deg. cent. in the sense that the calcium is vaporized and decomposes CO to again precipitate CaO, is one of the actions similar to the fumes in smelting furnaces which accounts for a heavy loss of metal at temperatures not ordinarily capable of producing vapors. When nitrogen is inserted in a reaction of this kind, there are immediately formed complex carbon-nitrogen compounds, but the action of the oxygen present is to dissociate these, allowing the nitrogen to combine into the molecular form and the metal to precipitate from the fume as a minute particle of metallic oxide, the carbon precipitating as amorphous carbon in the form of soot, as all of these reactions liberate a large amount of energy. The temperature of these reactions is from 1,500 deg. cent. to 2,000 deg. cent., and is therefore well within the range of combustion methods if the combustion could be in contact with the substances as in the blast furnace, but the presence of the oxygen necessary for combustion prevents the formation of nitrogen compounds.

The effect of partial pressures in these reactions is of fundamental importance. The active mass of a solid is constant, and hence at the boundary surface where the solid and gases meet there is a high velocity of reaction. Equilibrium will be produced either by the solid forming a coating of the compound which will place it in equilibrium or by the pressure of the gases generated from the reaction producing a condition of equilibrium. Taking the familiar calcium carbonate reaction as an illustration,

$$CaCO_3 \rightleftarrows CaO + CO_2$$

There being two substances in the solid state and one in the gaseous, the equilibrium constant K will be

$$K = \frac{CaO \times CO_2}{CaCO_3}$$

where CaO and $CaCO_3$ are the very slight vapor pressures of the solids; that is, the sublimation pressures, which in practice are too small to measure. The pressure of the CO_2 will be practically the total pressure, and as this varies, the velocity constant K will vary and hence for any temperature there is but one pressure for equilibrium. LeChatelier measured the temperatures and pressures of the above reaction over a wide range and found a variation in the temperature necessary to produce the reaction of from 547 deg. cent. at 27 mm. pressure to 865 deg. at 1,333 mm.; or in other words, equilibrium could be produced through a range in temperature of 60 per cent, and at one point a change of two degrees necessitated a change in pressure of over 10 per cent in order to restore equilibrium. Rothmund found the equilibrium pressure of CO in the carbide of calcium reaction to be 250 mm. at 1,620 deg. cent. If the CO pressure was raised above the equilibrium figure at this temperature, CO was absorbed and no carbide was formed. By inserting inert gases so the CO was diluted and its partial pressure reduced, the temperature of the formation of carbide was varied over 20 per cent. These results all indicate that for the nitrogen reactions must not only be subject to accurate temperature regulation, but the partial pressures must be controlled, and it is probable that definite zones of reaction must be maintained. The present commercial applications such as the Serpek and cyanamid processes prepare the compounds of nitrogen by causing the nitrogen to react largely with the solid masses and thus avoid many of these complications due to the vapor processes, or variable minute pressures of sublimation.

By substituting the resistance furnace for the arc and reducing the metals in the presence of nitrogen, thus forming nitrides or forming carbides, and treating these in the presence of nitrogen, there have been developed a number of processes which have been commercially applied.

III—Description of Processes.

Three processes which have been commercially applied for directly preparing nitric acid from atmospheric nitrogen are: First, Birkeland-Eyde; second, the Schonherr, and third, the Pauling. These are diagrammatically shown in Figs. 2, 3 and 4. Fundamentally all operate on the same principle of forcing air into intimate contact with a high-tension arc and withdrawing the product nitric oxide, NO, as directly and rapidly as possible in order to reduce the amount of decomposition of the resulting product. As these processes have been repeatedly described in detail in the technical press, we will confine our attention to general comparisons.

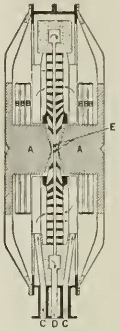

Fig. 2.—Birkeland-Eyde
A, core; B, windings, C, gas entrance; D, exit.

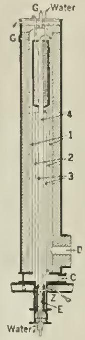

Fig. 3.—Schonherr Furnace.

Birkeland-Eyde Process. The Birkeland-Eyde furnace, illustrated in Fig. 2, has been the most extensively used. Its most distinctive features are the use of the magnets *A*, which distort the arc into a series of great wheels of flame, extending radially outward from the electrodes *E*, located normal to the paper in Fig. 2. The air enters through the conduit *C* and is distributed to the arc through the holes in the firebrick lining. The products are withdrawn from around the periphery at *D*. The voltage of 10,000 volts is reduced by an inductive reactance coil to about 5,500 volts across the electrodes. The alternating current of 50 cycles establishes the arc across the *U*-shaped water-cooled electrodes *E*, spaced about 0.3 in. (8 mm.) apart, and a flow of current takes place across this ionized path, the electrons formed being repelled by the intense magnet field of the direct-current magnets, *A*, and their discharge radially outward causes the arc stream to follow until it is deflected outward in a great semicircle. As its length is thus increased, the potential across the electrodes rises and a second arc is established, the effect being to make a series of rapidly expanding arcs which are expanded across the entering air spaces. As the arcs travel radially outward, the contact of the ionized arc stream with the incoming air disrupts the nitrogen molecule and causes the formation of NO, and the gaseous products travel rapidly to the periphery of the furnace, where they are withdrawn at an average temperature of about 1,250 deg. cent. The earlier Eyde furnaces were of 300 kw. capacity and gave a concentration of about 1.5 per cent NO and a yield of about 500 kg. of nitric acid per kw. per year. The more recent furnaces are of 3,000 kw. capacity and give concentration of about 2 per cent NO and a yield of 580 to 600 kg. of nitric acid per kw. per year, or 65 to 70 grams of nitric acid per kw.-hr.

Schonherr Process. The Schonherr furnace (Fig. 3) consists of a long iron pipe, having an electrode *E* inserted in the bottom, and the tube itself is the other electrode, the distinctive feature of the process being that an alternating current at 4,500 to 5,000 volts maintains an arc of from 23 to 25 feet (7 m. to 8 m.). The furnace is started by forming an arc from the lower electrode to the wall of the iron pipe by means of a lever *Z*, a blast of air is then admitted to the pipe, whereupon the ionized gases are caused to ascend and carry with them the arc stream. In this way the arc is caused to travel toward the upper end of the tube, where it is maintained. In practice, the air stream is admitted in a tangential direction, causing a whirling motion to be imparted to the air surrounding the arc; this creates a vortex motion, causing the arc to be surrounded by the cooler air and thus protects the iron pipe which is wholly unlined. The rapid passage of the air maintains an ionized path for the arc stream, and the arc burns quietly. The products are withdrawn from the upper end and pass downward through the passes *I* to the outlet *D*. Previous to being withdrawn they are cooled by the water cooler and are further used to preheat the entering air. The temperature of the exit gases is about 850 deg. cent. Provision is made for preheating the air by passing it upward in the space 2 of the casing and then downward to a point opposite the electrode. The largest furnaces are of 800 kw. capacity and maintain an arc about 23 ft. (7 m.) long. They give an NO concentration of about 2.25 per cent and a yield of 550 to 575 kg. per kw.-year or 65 grams per kw.-hr.

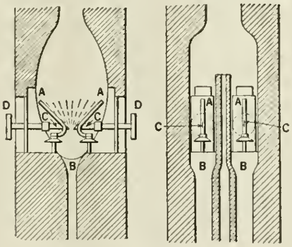

Fig. 4.—Pauling Furnace.

Pauling Process. The Pauling furnace (Fig. 4) establishes an a-c. arc of 4,000 volts between two curved horns, much after the pattern of the horn type lightning arrester. This arc when established is driven upward by a blast of air admitted at *B* and is disrupted by the diverging horns. A sheet of arc flame is maintained by re-establishing a new arc, as the previous one is elongated. The effect is to create an arc flame about 30 in. (75 cm.) high and to have this flame in intimate contact with the rapid moving air used to blast the arc flame. Two furnaces are usually operated together, and to assist in a rapid cooling of the products, a portion of the previously heated or partially cooled discharged gases are admitted to the top of the furnace. The arc is established by the high voltage breaking down the gap between narrow blades *C*, located in the horn gaps, and as these wear away, they are continually advanced by the adjustments *D*. The percentage of NO obtained is 1.25 to 1.5 per cent in the 400 kw. furnace, while the yields are 525 to 540 kg. per kw.-year or 60 grams per kw.-hr.

Power Factor and Electrode Wear. In all these processes where the arc is distorted the power factor is about 70 per cent, being about 5 per cent lower in the Schonherr type, apparently due to inductive effects of the iron pipe surrounding the arc. In both the Pauling and Schonherr furnaces the electrodes are adjustable and the air blast plays directly on the electrodes, necessitating this adjustment and also means of easy renewals. The Pauling blades last less than twenty-four hours. The Schonherr electrode is a straight rod of iron and is fed upward as it burns away. The Eyde water-cooled copper pipe not being directly in the path of the air blast lasts three to four weeks. In the operation of both the Eyde and Schonherr furnaces a furnace is placed on each separate leg of the three-phase circuit, so that six wires are used for each generator. In the installations that have been made the furnaces are connected direct without transformers, and as no parallel operation of generators is attempted, a large number of cables are required between the power house and the furnaces.

Efficiency and Losses. It will be noted that notwithstanding the radically different types of these furnaces there is not a wide divergency in the yields, the Schonherr furnace showing the highest concentration of NO, while the Eyde probably produces a slightly higher output per kw.-hr. All of these concentrations indicate that the maximum temperature of the arc is not utilized, but is very considerably reduced by the large amount of air admitted. If the temperature of the arc is raised by admitting less air, there is a heavier decomposition of the products, and all products are heated to a higher temperature with a corresponding loss, the net result being a lower yield per kw.-hr. As the yield per kw.-hr. is of fundamental importance, adjustments are governed accordingly. The concentration of NO affects directly the apparatus for recovering the products, such as the absorbing towers, and the lower the concentration of NO the greater the losses from heating the inert gases. The furnace efficiency will largely be determined by this factor. Let us take for example a concentration of 1.75 to 2 per cent NO and examine the distribution of heat. If we take the specific heats of a molecule of the diatomic gases as constant, there will be no difference in the specific heats per molecule of N, O or NO, and taking a standard value for this, we may calculate the heat energy expended. Let us assume, following Haber, that for a change of temperature *t*. the specific heat per molecule will be

$$6.8 + 0.0006\, t$$

The gaseous products heated in the furnace with 1.75 to 2 per cent NO concentrations will have, from Nernst constants, an absolute temperature of about 2,500 deg., and the air would have an initial temperature say of 27 deg. cent. or 300 deg. absolute, so the arc would raise the temperature of the 100 molecules through 2,200 deg., or,

$$\text{sensible heat} = 100\ (6.8 + 0.0006\, t \times 2{,}200)\ 2{,}200 = 1{,}786{,}400 \text{ calories}$$

As two molecules of NO require a latent heat of formation of 43,000 calories, the total heat will be 1,829,400 gram-calories; and as one watt hour equals 860 gram-calories, the energy represented will be equal to 2.12 kw.-hr. for two gram-molecules of NO. Taking the atomic weight of N as 14 and of O as 16, the gram-molecule of NO will weigh 30 grams, so 2.12 kw.-hr. will form 60 grams of NO.

If we mix this NO with air and water it will form nitric acid without requiring a further expenditure of energy, thus,

$$2NO + 1\tfrac{1}{2}\, O + H_2O = 2HNO_3$$

and the 60 grams of NO will then become 126 grams of HNO_3; the production of nitric acid will then be 126 grams per 2.12 kw.-hr. or 59.4 grams of HNO_3 per kw.-hr. Of this expenditure of 2.12 kw.-hr. the formation of the nitric oxide utilized

$$\frac{43000}{1{,}829{,}400} = 2.35 \text{ per cent}$$

and the sensible heat imparted to the active gases to raise their temperature to form two molecules of NO required 35,728 calories, so this represented

$$\frac{35{,}728}{1{,}829{,}400} = 1.95 \text{ per cent}$$

while the heating of inert nitrogen and oxygen, or that portion of the air which was not utilized, but which was heated to the furnace temperature, was represented by

$$\frac{1{,}750{,}672}{1{,}829{,}400} = 95.7 \text{ per cent}$$

These calculations, while open to some criticism on account of the uncertainty of the figures for specific heat and its change with temperature, closely approximate the conditions, and indicate that low concentrations of NO, when formed from thermal reactions, are extremely wasteful. If concentrations of 10 per cent NO are obtained with temperatures of 4,200 deg. to 4,300 deg. cent., the yields may be increased to 135 to 140 grams of HNO_3 per kw.-hr., but the greatest saving in energy will result in utilizing other than purely thermal energy. While thermal energy may be produced more cheaply directly from fuel, its temperature possibilities are again limited by the inert gases of combustion if air is the source of these.

Hausser has commercially applied a process for utilizing coke oven gases by means of an explosion bomb. The amounts of excess gases may be limited, and the intimate mixture of combustible and oxygen due to pre-compression of the charge permits of high combustion temperatures being reached. Fig. 5 shows this bomb having a capacity of 1,600 cu. cm. The gases, either illuminating or coke oven gases, enter through the inlet after previously exhausting the air by means of the air pump outlet. Means are provided at *A* for injecting under high pressure a spray of water to cool the products as quickly as possible. The ignition takes place at 2 by means of a high-tension spark, and the explosion is propagated outward from this point and the vapor condenses on the enamel lining of the bomb.

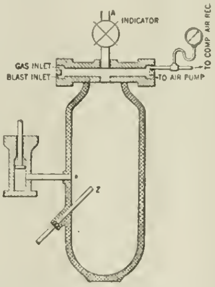

Fig. 5.—Hausser Process.

With this device Hausser obtained a temperature of 2,100° K. and concentrations of NO of 0.5 per cent. The temperature calculated from the assumed figures for specific heat indicated a concentration of 0.3 per cent for equilibrium by the Nernst calculation, and Hausser sought to explain this increase of yield as due to a chemical reaction induced by photo-chemical effects similar to the ionization by the ultra-violet or actinic rays of light. The maximum yields were 99 grams of HNO_3 per cu. m. of gas, or equivalent to 6.2 lb. of HNO_3 per 1,000 ft. of gas. A commercial plant on this system has been installed in Germany. This low concentration of NO greatly complicates the commercial application, as the absorbing devices are more cumbersome and the percentages of loss are higher.

Method of Utilizing NO. All of the above nitric acid processes utilize the reaction

$$2NO + O_2 \rightleftarrows 2NO_2$$

which is an exothermic one for the formation of the peroxide, and if the temperatures are controlled, side reactions can be prevented and equilibrium can be maintained with only a small percentage of NO remaining. The gases, after leaving the furnaces, are usually carried through waste heat boilers where 50 to 60 per cent of the heat is utilized for steam production. They are then cooled in aluminum pipe coolers and allowed to enter a gas holder, where time is given to form the peroxide. The products then enter counter current absorption towers, where the reaction with water forms

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

the nitrous acid, HNO_2, is further oxidized and utilized to form HNO_3 in contact with the excess oxygen in the gases and with the absorbing water. The final recovery is usually made by circulating the gases through two towers of weak alkaline solution, such as sodium carbonate, and this is converted into sodium nitrate and into sodium nitrite, and recovered by evaporation; the final products are a combined nitrate-nitrite of sodium. A normal circulation over three absorbing towers gives an acid of about 30 per cent concentration, but this can be increased to 45 to 50 per cent by recirculating over the first tower. Further concentrations are usually made by evaporation. All of these processes are simplified by increased concentrations of NO in the initial reaction. About two to three per cent of the original NO is discharged in the waste gases from the absorbing towers. It will be noted that one great advantage of these processes is that they require the handling of only air, gas and water up to the time the nitric acid is formed in the absorbing towers, so that the simplest handling devices suffice and the labor is a minimum; also no chemicals are required until the final washing with the alkaline solution in the absorbing towers, and this may be a cheap solution, such as lime water, if conditions make it desirable.

Cyanamid Process.—The very low yields, representing less than 5 per cent of the energy expended and amounting to 65 kw.-hr. per kg. of N fixed, naturally have turned attention to chemical reactions as a means of increasing the yields. One of the most important of these is the process for making cyanamid, $CaCN_2$. As a separate paper is to be presented here covering this subject, we will only generalize.

The endothermic reaction and the heating of the materials entering into the calcium carbide reaction have an approximate theoretical value of 3.1 kw.-hr. per kg. produced, whereas it requires about 4 kw.-hr. to produce a kg. of 85 per cent calcium carbide in the best practice. For 100 per cent carbide it would require 4.7 kw.-hr., and the efficiency is therefore,

$$\frac{3.1}{4.7} = 66 \text{ per cent.}$$

The union of carbide and nitrogen is exothermic when a sufficient temperature is reached, so the actual expenditure of energy for this reaction is not in excess of 0.1 to 0.2 kw.-hr. additional for the fixation of the nitrogen. We require further the preparation of the nitrogen and the grinding of the carbide to prepare it for the nitrogen treatment. The cyanamid can be used directly in the fertilizer industry, but for use in the chemical industries it must be decomposed to form ammonia; or, if nitric acid is required, it must be made from the ammonia by some process such as the Ostwald contact process. We may figure, however, that the yield for a given amount of electric energy, which amounts to about 16.6 kw.-hr. per kg. of N fixed, is from four to five times the yield of the direct nitric acid processes, while offsetting this is the cost of preparing the nitrogen, the cost of chemicals, the handling of materials at high temperature and the many factors making up manufacturing costs.

The Serpek Process.—The Serpek process is typical and has been quite extensively introduced commercially. The reaction is represented by the equation

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$

The reacting temperature for best results is claimed to be 1,800° to 1,900° C., but no effort is made to define the equilibrium conditions, and it is very evident that where CO enters so actively into the reaction, the temperatures can be materially altered by a change in the partial pressures of the N and CO. One of the most interesting features of this process is that the impure Al_2O_3 in the form of bauxite is fed into the furnace together with coal and the sensible heat is therefore partially derived from the coal. Neglecting the specific heats of the solids, the endothermic reaction requires three kw.-hr. per kg. of aluminum nitride having an approximate content of 26 to 34 per cent N; it would require therefore 9 to 10 kw.-hr. per kg. of N under the best conditions if the coal and producer was were capable of supplying all the heat energy required to produce the required temperature in the gaseous and solid products. In the case of cyanamid it requires about 4 kg. of high-grade carbide per kg. of nitrogen, or a kg. of N requires 16 kw.-hr. under favorable conditions and about 0.2 kw.-hr. for heating the carbide against 10 to 12 kw.-hr. in the Serpek process. If all energy were supplied from the electric source, the Serpek process would require practically the same electrical energy as the cyanamid process.

There is a distinct advantage in being able to use producer gas in place of preparing purified nitrogen, and there is a further advantage in conducting the process with one operation. In practice Serpek uses a revolving barrel furnace of the resistance type, the resistance consisting of a squirrel-cage construction which continually agitates the material as it passes through. In all nitride reactions this is essential, as the materials become coated with a covering which protects the interior and prevents further absorption of nitrogen. Serpek feeds bauxite and coal from a producer type of furnace into this revolving electric furnace and the sensible heat is thus utilized to heat the material as it travels to the electric furnace; the product is discharged from the electric furnace as aluminum nitride, with a content of 26 per cent to 34 per cent N.

The aluminum nitride can be treated with steam and the N converted into ammonia, or the ammonia may be converted into nitric acid. Serpek claims a process for converting the nitride directly into nitric acid, but no details are available. One drawback to using bauxite is that the resulting aluminum oxide is more difficult to use than the impure bauxite and the process does not work as economically. It is probable that some cheap catalytic agents may be found to substitute for the bauxite, but otherwise the Serpek process should necessarily find its greatest application in connection with the reduction of aluminum.

Haber Catalytic Process.—One other process which has attracted marked attention on account of the scientific eminence of its inventor, as well as the commercial results obtained, is the Haber process for the synthesis of ammonia directly from its components N and H. This means that there must be a supply of these elements available or they must be cheaply produced. The reaction is an exothermic one producing 11,000 calories per gram-molecule, so the problem is not so much the eneregy consumption as the peculiarities of the reaction

$$N_2 + 3H_2 = 2NH_3.$$

The ammonia formed is practically decomposed at 750° C. It has been difficult to get any substance to react with the N at this low temperature, and, while the nitrogen was made active toward many substances, it was easy to decompose the resulting NH_3 into its constituent molecules, and all yields obtained were too low to justify commercial results. Haber's success seems due more to ingenuity in constructing his apparatus and to the discovery of a suitable catalyzer than to any departure from previously known principles. The fact that one molecule of N and three of H form only two molecules of ammonia indicates that the volume occupied by the ammonia will occupy only one-half the space occupied by its constituent gases, and hence this contraction of volume will be assisted by pressure. Haber increased the pressure on the reacting gases to 200 atmospheres, and as a catalyzer he used uranium. He found at 500° C. he could react on the nitrogen and upwards of 8 per cent of ammonia could be formed before equilibrium took place. By using limited amounts of N and an excess of H the equilibrium pressures were adjusted well within the decomposition limits of temperatures, and by withdrawing the gases from the catalyzer as they reached equilibrium the process was made continuous. The fact that decomposing ammonia creates a most destructive corrosive agent had to be met, and the retorts had to be made strong enough to stand the effects of the high pressure and also possible explosion, as hydrogen compressed to 200 atmospheres and heated to 500° C. is a most active agent in the presence of impurities such as oxygen, sulphur, etc. The retorts can be made of very moderate size and a number of them used, and by heating internally with electric resistance the shells are not subjected to the effects of temperature, so the process seems to have met with very pronounced technical success. The consumption of energy for heating the gases is very slight, as the exothermic reactions will compensate largely for the heat required to release this.

The preparation of the N and H and the compression to 200 atmospheres will represent the greatest costs of production. It will be noted that all products are handled in the gaseous condition, being most favorable for low labor costs. The ammonia is extracted from the mixture of N and H by slightly cooling the gases until the point of liquefaction of ammonia is reached and the ammonia condenses out. The remaining gases are passed back to the retort without sacrificing the original pressure of compression. The work done on the gases is thus reduced to a minimum, and equilibrium can be continually disturbed by withdrawing the products without heavy losses. This process involves the expenditure of approximately 1.5 kw.-hr. per kg. of N and therefore represents the lowest consumption of energy of any of fixation processes.

From an engineering point of view the various processes must be considered from other than the technical standpoint, the question of particular application being the guiding consideration in most cases.

IV—THE ECONOMICS OF NITROGEN FIXATION.

Fertilizers.—In considering nitrogen fixation and its relation to fertilizers we must remember it is only one of the three important ingredients of fertilizers, the other two being phosphorus and potassium. It is possible to obtain nitrogen from the atmosphere and transfer it to the soil by means of nitrifying bacteria, which may be cultivated by such plant life as the legumes, to which family belong the clover and alfalfa. These plants have a nodule on the stem which is the seat of the bacteria activity, and if the plants containing this nitrogen are returned to the soil, the soil may be enriched in nitrogen, but the crop must be sacrificed or partially so. When it is not desirable to plant these nitrifying crops, recourse must be had to nitrogen in the form of fertilizer. Unfortunately all crops deprive the soil of fertility, and in the case of phosphorus and potassium converted into the crops, these must actually be replaced or barren soil will eventually result. Each soil must be treated for the particular crop it is to bear, and usually there are fixed mixtures which become standard for various crops. These mixtures contain the nitrogen, the phosphorus and the potassium in varying amounts. The output of nitrogen from a chemical works would ordinarily be shipped to these fertilizer manufacturers unless the chemical works desired to manufacture the mixed fertilizers.

Of all the processes we have considered, the cyanamid is the only one which manufactures a product which is in a form to go into the fertilizer market direct. The nitric acid processes must unite the acid with some alkaline base such as sodium, lime or ammonia, and the ammonia process must unite the product with an acid such as sulphuric or nitric. The nitride processes can hardly afford to ship the nitride, as it is combined with an ore or base such as aluminum oxide, which may be more desirable in the aluminum industry, as the fertilizer industry will pay only on a nitrogen basis.

Price of Nitrogen.—In general the price of combined nitrogen, as we have seen, is fixed by the price of Chile nitrate. Thus if this sells for two cents per pound and contains 15 per cent N, the price per pound of N is 13.2 cents, and this in turn would make the price of ammonia sulphate, having 21 per cent of nitrogen, 2.7 cents per pound. These have been current prices. In considering the production of nitrogen products, it would seem that, while these prices control nitrogen for the fertilizer industry, it would be desirable to produce if possible products which are manutactured from these crude products and thus avoid competition with the natural products direct. Nitric acid of commerce is manufactured from soda nitrate by treatment with sulphuric acid, about 72 per cent of the sodium nitrate being nitric acid. As the by-products of this operation only partially pay the costs, the manufacturing costs leave the nitric acid with a value of 50 per cent over the value as nitrate. Hence a chemical works could afford to produce nitric acid when they could not afford to add a manufacturing cost to produce a fertilizer from the nitric acid and then sell it in competition with the crude Chile nitrate.

A large portion of the phosphate rock of this country is treated with sulphuric acid to form the so-called superphosphates. If nitric acid is used in place of sulphuric acid, the superphosphate can be produced at the same time as a fertilizer of lime nitrate, or, if preferred, a high concentration of phosphoric acid can be produced from lower-grade phosphate rock. Industries of this kind promise more favorable results commercially than does the direct production of fertilizer. If low-grade products are manufactured at close prices, a very large volume of business is a necessity, and works of this character and magnitude are more apt to be a result of successful development rather than an initial venture in a field beset with uncertainties as to the profits and the chances of a development of other processes reducing these if they are problematical.

Costs of Making Products.—Let us consider more in detail some of the costs. We may assume approximately that the labor and repairs in furnace room and absorbing tower will cost \$10 per ton of nitric acid, and if nitric acid is selling for \$60 per ton, we have a margin for power costs, interest, general expense, etc., of \$50, and if we produce 500 kg. of acid per kilowatt year, it will require two kw.-yr. per metric ton or \$25 per kilowatt-year, and we must absorb all interest charges and general expense in this. If the yield can be made 550 kg. per kilowatt-year and we can sell for \$60 per short ton, we will require 1.8 kw.-yr. or \$28 per kw.-yr. We must assume that the product does not have to be packed for shipment and that there are no selling costs involved, and we must figure on an output so that our units may be large enough to bring the investment in plant down to \$80 per ton of acid, so the annual charge may be \$8 or net \$20 per kilowatt-year, and if \$5 are allowed for general expense, the best we can do will be about \$15 per kilowatt-year.

We see it would be hopeless to attempt to put this acid into a product to compete with the fertilizer prices, for they are some 50 per cent lower in selling price, and it will involve a cost for some raw material to mix with the acid, the cost of manufacture and a packing and shipping charge. We must then abandon any idea of making fertilizer from nitric acid prepared by the direct oxidation of atmospheric nitrogen in the electric arc until such time as we can improve the very low efficiency due to the thermodynamic limitations of the reaction. We can only hope to utilize this process in the manufacture of nitric acid coupled with some other product which will procure for it a higher price. There is, for example, a limited demand for the nitride of sodium $NaNO_2$ used in the dye industry, and this is manufactured by reducing nitric acid with molten lead, thereby adding another manufacturing operation to the acid cost. This nitrite may be cheaply made by taking a mixture of NO and NO_2, such as we would have in parts of the system, and passing it into water or sodium hydroxide, thus

$$NO_2 + NO + H_2O = 2HNO_2$$

or,

$$4NO + 2NaOH = N_2O + 2NaNO_2 + H_2O$$

and this process would produce a product selling for four to five cents per pound. We must remember, however, that the price of nitric acid is not a fixture and that a cheap combined nitrogen fertilizer will cut the price of sodium nitrate and hence the price of nitric acid. We are confronted then with the fact that all processes will be affected by the success of any one process that is a large enough success to affect the market conditions of combined nitrogen and upset the ruling prices in the fertilizer industry. It is useless to look only to cheap power as a solution of this problem, as the real solution is in the improvement of processes.

Let us roughly compare the power requirements of the processes as we have outlined them above, and we find

Direct oxidizing of atmospheric nitrogen 5 per cent efficiency, yield at 550 kg. per kw.-year, requires per kg. of N....................................	65 kw.-hr.
Cyanamid process 66 per cent efficiency in carbide 1 per cent loss in heating to combine with N., requires per kg. of N........................	16.6 “
Also preparation of N.	
Aluminum nitride using coal to heat products to temperature of reaction requires per kg. of N..	12 “
Catalytic method of combining N and H to form ammonia, requires per kg. of N................	1.5 “
Also preparation N and H, refrigeration, and compression to 200 atmospheres.	

The general tendency abroad in figuring the cost of water power is to give only the operating costs, and from this one sees costs of producing power figured at from 50 cents to $1.00 per kilowatt-year, and in using these figures erroneous ideas have been widely circulated. In this country it has been standard practice to consider the investment in the power plant; that is, the cost of the development and the property as fixing very largely the cost of producing the power. It is quite common to have labor and supplies cost not more than one dollar per kilowatt-year, but this would not be considered as representing the cost of the power. Where a chemical industry owns the hydroelectric power plant as well as the chemical works, the foreign practice is inclined to consider the investment as a whole and apportion the costs of operation to the various departments, while interest on the capital is charged to the profits. The costs of producing power are therefore uniformly much lower than we are accustomed to figure on. There are many plants in operation in the chemical industries abroad whose real costs of producing power are no lower than many of the more favored locations in this country.

Off-Peak Loads.—One of the chief interests in the chemical utilization of electrical energy is centered in the possibilities of off-peak or off-season loads, as American plants generally have a certain proportion of power which can be disposed of to better advantage than selling the entire output as low-priced power to chemical industries. This off-peak power is difficult to utilize in furnace work, where the cooling of the furnace and its charge is an important factor both from the standpoint of cost and of output, and again, adjustments may be so disturbed from an interrupted output as to be absolutely impracticable. One of the possible solutions for off-peak utilization appears to be in the adoption of some system where fuel is also utilized and the radiation losses are not excessive under conditions of banked fire when the electric portion of the heat energy is not in use. Some of these combination processes may promise a solution of the off-peak load situation more attractive than the straight electric furnace, which is difficult to cool down entirely without unduly affecting the conditions. In all plants the volume of output is the determining factor in absorbing the general overhead charges, and any intermittance must diminish output with its accompanying disadvantages.

If the furnace could be operated on the off-season load and its product stored, and the chemical works utilizing this product could operate on a normal schedule, this would form one solution; or another would be, if by chance the off-season power were available at the time the greatest demands were to be met, such as preparing a fertilizer product at the season of fall rains for the early spring delivery. All of these plans, however, suggest the necessity of operating at least a portion of the plant continuously in order to meet fixed charges and preserve an operating organization. If the chemical works require a moderate amount of power for its processes in year-around operation and only its surplus for manufacturing its crude material at the off-season peak, it promises the greatest possibilities.

The future of nitrogen fixation is alluring and promises many developments along lines other than those we have considered, but already the market has felt the effects of these various processes, and instead of nitrogen being figured at 13 cents per pound, it is confidently predicted it will very shortly find its level at a selling price of about 8 cents, making a cost of production of 5 to 6 cents per pound and thus reducing sodium nitrate to about 1.33 cents per pound, or approximately $30 per long ton, and the lower-grade mines will feel this and be forced to curtail.

It therefore seems very certain that before 25 years shall have elapsed since Sir Wm. Crookes made his memorable address, the Chile nitrate beds will have vastly curtailed their production, not from exhaustion, but from the inroads made by the onward advance of chemical and electrochemical engineering.

POTASH FROM FELDSPAR.*

The cost in Germany of producing one unit of potash (20 lbs. of K_2O), in the form of commercial "muriate," is known to be less than 15 cts.; adding all handling and sales costs, and a reasonable return upon the money in use, the cost per unit ex-ship U. S. Atlantic seaboard does not exceed 30 cts. Hence, if at the close of the present European war Germany still remains a member of the family of nations, and plies its foreign trade as heretofore, no potash mine, method, or process having a producing cost of 30 cts. or more per unit, can possibly survive German competition.

Feldspar deposits of vast extent have been located, having an average run-of-mine composition as follows:

	Per cent.
K_2O	11
Na_2O	2
SiO_2	70
Al_2O_3	17

The soda has no value, as the cost of separating soda from potash would probably exceed the market worth of the recovered soda. Assuming potash worth f. o. b. factory 29 cts. per unit, and alumina, 100 per cent pure and free of iron and silica, three-fourths of a cent per pound, and the silica 25 cts. per short ton; the total values in one short ton of feldspar aggregate \$5.92. It is true that alumina of the purity indicated cannot be purchased at this time for less than 3 cts. per pound; but that price is the result of something of the nature of a "gentleman's agreement." Alumina produced in any quantity must, to find a market, displace bauxite, and must be prepared to meet bauxite prices.

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*From The American Fertilizer.

The bald facts seem to imply that no feldspar potash recovery process is worthy of investment support unless it is able to operate at a cost of \$5.92 per short ton of feldspar, including upkeep, and an attractive return on the investment involved.

There are very many feldspar recovery processes and prominent among them are those using spar as a substitute for clay in making Portland cement. This general project has much in its favor, because of the unlimited market for the cement by-product. However, under average conditions, the cost of materials, clay and lime, in Portland cement making amounts to less than 3 cts. per 100 lbs.; hence, for making such cement, one short ton of feldspar has an apparent value of:

11 units of potash at 29c	\$3.19
17.4 cwt. silica, etc., at 3c	.52
	\$3.71

Against this must be charged the cost of the spar and process for extracting the potash; and a reasonable profit on the capital invested in the potash recovery process. The values are discouragingly low for the purpose.

It seems evident that a commercially successful feldspar process must not only effect the recovery of the potash, but in doing so must create other industrial values. To illustrate: a mixture of feldspar and potassium chloride heated to 1050° C. produces potassium silicate and aluminum chloride, which latter is of course removed in process by sublimation. The potassium silicate is easily and cheaply converted to potassium carbonate and a pure iron free silica. The aluminum chloride may be easily converted to alumina and carbon oxychloride, which reacts with feldspar to make potassium chloride, etc.; that is, the chlorine may become largely cyclic. This process, while vastly more hopeful than the cement or alkali extraction processes for decomposing feldspar, still verges sharply on the limit of cost and provides a margin of safety too narrow to justify investment capital.

There remains possible the utilization of feldspar as a decomposition phase in producing commercial soda ash, or caustic, and this method has been carefully examined by trained investigation. The results are given in brief in the following description.

FELDSPAR-SODA ASH PROCESS.

A mixture of phosphate rock and common salt is heated to 1100° C. in a muffle furnace, in which an inert gas such as carbon dioxide is slowly flushed through the furnace chamber. The phosphorus and chlorine are removed by volatilization, leaving the soda and lime as furnace residue. The reaction may be stated in proportional formula, as follows:

$$Ca_3P_2O_8 + 10\,NaCl + 2\,CO_2 = 3\,CaO + 5\,Na_2O + 2\,POCl_3 + 2\,COCl_2$$

This reaction is governed by no time factor other than fuel economy, hence the operation may be continued at will, and a very high reaction efficiency realized.

From the furnace residue the soda is extracted by leaching and is marketed either as caustic or as soda ash, for which purpose the waste fuel gases are utilized; the furnace fuel is producer gas. This is the first step, and a low cost sodium salt is changed to forms in which its industrial value is tripled.

The second step consists in passing the phosphorus and carbon oxychlorides over feldspar heated to 600° C. in a muffle furnace. By this treatment the potash and alumina in the feldspar are converted to chlorides, and the alumina chloride is volatilized and passes out of the furnace. The furnace residue consists of silica and potassium chloride, and the latter is extracted by leaching and is converted to the commercial "muriate" by utilization of waste furnace gases. The phosphorus, of course, becomes P_2O_5.

The volatilized aluminum chloride is separated from any iron chlorides present by simple fractionation and is then volatilized in the presence of carbon dioxide or sulphur dioxide, through a baffled furnace chamber heated to 800° C. (about the dissociation temperature of carbon oxychloride), and alumina and carbon oxychloride are formed, thus:

$$2\,AlCl_3 + 3\,CO_2 = Al_2O_3 + 3\,COCl_2$$

and the carbon oxychloride is returned to process. As a final product all of the potash becomes chloride and the alumina of the spar is separated as such and free of silica, alkali or iron.

Assuming a plant decomposing 40 short tons of tricalcium phosphate per day, the materials required assuming both phosphate and feldspar are used in 5 per cent excess, are as follows:

Phosphate rock, 70 per cent	53 long tons
Common salt	76 short tons
Feldspar	455 short tons

The daily products would be:

	Lbs.
Phosphoric oxide, 100 per cent	36,570
Soda ash, 97 per cent	133,910
Potash chloride, 50 per cent K_2O	190,646
Alumina, 100 per cent	147,000

The furnace fuel may be closely approximated by adding to the thermochemical heat summation of each reaction the sensible heat in the reaction products at the reaction temperature. For all the reactions involved, assuming a fuel coal of 3,000 kilogram calories value per pound, and an efficiency of 15 per cent for the high temperature furnaces and 20 per cent for those of low temperature, the total fuel required per day amounts to 178 long tons.

Plant and operation data are approximately as follows:

The high temperature furnaces treat daily 130 tons of charge, and assuming fairly large furnaces, with two always in reserve, 12 will be required. The cost of this equipment emplaced should not exceed $90,000, and the daily operating labor should not exceed $60. The low temperature furnaces treat daily 460 tons of charge, of which about 80 tons are given a second treatment. About 16 furnaces will be required, involving a plant outlay of about $75,000, and a daily operating labor charge of about $30.

The gas producers burn 180 tons of coal per day and will cost about $40,000, with a daily operating labor charge of $20. The soda ash plant will cost $40,000, with a daily operating labor charge of $20.

The power and milling plant will cost about $50,000, with a daily operating labor charge of $25. There should be ample waste heat to generate all the steam required.

Buildings and land, with total miscellaneous equipment, including office and laboratory with fittings, will cost about $80,000. The daily miscellaneous labor charge, covering incidental work, etc., will not exceed $50.

The daily management and supervision may be approximated as follows: Superintendent, with two assistants, $26; chemist and assistant, $9; three mechanics, $12; clerical services, $10; total, $57.

The total plant cost should not exceed $375,000 and the daily pay roll $262.

The annual general charges should not exceed:

Plant depreciation at an average of 10 per cent	$ 37,500
Insurance, taxes, etc	12,000
Supplies and office expenses	45,000
Executive and legal	10,000
Interest on stocks, at 5 per cent	15,000
Total	$119,500

The plant is assumed to have a producing year of 340 days, but an operating year of 360 days; that is, 20 days of each year are devoted to repairs and the training of men and machinery.

To the operating cost must also be added a certain proportion of about $50,000 to cover the usual cost of starting a new plant, training men and balancing machinery. This charge is properly an operating expense and is extinguished with its interest charge by even payments extending over a period of about six years; hence, to the annual operating costs for the first six years must be added about $10,000 yearly.

The following general summary of annual costs may be characterized as conservative:

Phosphate, 18,020 long tons at $5	$ 90,100
Salt, 26,180 short tons at $5	130,900
Feldspar, 154,700 short tons at $1	154,700
Coal, 60,520 long tons at $3.50	211,820
Payroll	94,320
New plant expenses	10,000
General accounts	119,500
Total	$811,340

Assuming a producing year of 340 days the annual value of products should be as follows:

Phos. oxide, 100 per cent, 6,208 tons at $40	$248,320
Soda ash, 97 per cent, 22,763 tons at $10	227,630
Alumina, 100 per cent, 24,990 tons at $15	374,850
Total	$850,800

Exclusive of the potash, this process indicates a profit of $39,460 yearly, which should amply cover all process rights, etc.

The potash produced per year amounts to 32,300 short tons of "muriate" of a grade corresponding to 50 per cent K_2O, and so far as factory costs are concerned may be written off as produced free of cost.

Phosphoric oxide (P_2O_5) is valued at 40 cts. per unit, and this requires explanation. This product would be recovered as phosphoric acid, H_3PO_4, of any desired concentration, and would be used to replace sulphuric acid in converting gaseous ammonia at by-product coke plants, etc., to solid form. The cost of sulphuric acid combined with one unit of ammonia as ammonium sulphate ranges from 30 to 50 cts., depending on the delivered cost of sulphuric acid; and as in ammonium phosphate, this sulphuric acid would be replaced by a trifle more than two units of P_2O_5; evidently, the *acid* value of P_2O_5 is about 15 cts. per unit, minimum. Deducting this from the 40 cts. per unit estimated value, leaves a fertilizer value of 25 cts. per unit of P_2O_5, a value markedly lower than any other source of water soluble phosphoric acid known at this time.

The limiting factor of this process is the consumption of alumina. For every unit of potassium oxide recovered, about 30 lbs. of alumina are produced. However, an independent source of iron and silica free-alumina at so low a cost as $15 per short ton would no doubt enable the price of metal aluminum to be cut in half, and thereby vastly extend the consumption of that metal. To do this it would possibly be necessary to foster aluminum producing industries other than those now in operation; probably not a very difficult undertaking if suitable alumina at $15 per ton is guaranteed.

[The above article is interesting in the presentation of some possibilities in potash production. In our opinion, however, some of the chemical reactions require verification. The operating costs are also very problematical.—Editor The Chemical Engineer.]

Chemical industrial companies newly established throughout Japan in 1914 amounted to 87, with $8,209,000 capital, showing a falling off of 56, with $671,400 capital as compared with 1913. Classified according to kinds of companies, there were 28 joint-stock companies, with $2,054,250 authorized capital, of which $602,000 was paid up; 46 limited liability partnership, with paid-up capital of $560,000, and 13 unlimited liability partnerships, with $58,000 paid-up capital.

PURIFYING PRODUCER GAS.*

By A. J. WALLACE.†

A recent issue of The Iron Age contained an article by C. A. Tupper, dealing with the removal of sulphur from producer gas through the medium of iron oxide. Mr. Tupper's remarks open up an interesting topic for discussion, and the writer wishes to say a few words on the subject.

For a considerable length of time the producers of illuminating gas in America have complied with the law and satisfied their customers by removing the sulphuretted hydrogen contained in their gas, varying from 1 to 10 grains per cubic foot, with hydrated iron oxide, largely prepared from borings and turnings. During the conversion from metallic iron to oxidized iron, considerable heat is developed, requiring careful watching and handling to prevent the production of a partly or practically dehydrated mass. Mr. Tupper mentions dehydrated material, which may prove efficient to a certain degree; but oft repeated experiments have demonstrated beyond doubt that the more completely the purifying oxide is hydrated the better it will answer the purpose for which it is intended, provided that other features of the material are in the right condition. In using the word hydrated, we are referring to water of combination, that is, moisture chemically combined with the oxide and not free moisture which is an entirely different proposition.

Several years ago, one of the largest illuminating gas companies in the United States began looking for material that would permit of a greater rate of flow or an increase in its output, without a corresponding increase in purifying capacity. The search settled on material in a finely divided state, and the company found what it was looking for in an oxide coming from abroad, which is known as precipitated oxide. The material in question, in addition to its high state of hydration is finely divided and in a colloidal state. In this connection, I desire to quote from a report prepared by the Institute of Industrial Research, Washington, D. C.:

"It is a well recognized fact that in gas purification the purifying value of iron oxide is dependent upon a high state of hydration and for a given weight of oxide is proportional to the area of reacting surface exposed to the gas. First of all, it is necessary that the oxide be in a hydrated state, as an oxide which has been deprived of its water of hydration, for example an ignited oxide, is practically inert. The superiority of sample L is undoubtedly due to its higher state of hydration and higher percentage of very fine material, which offers a large reacting surface area when distributed over wood shavings or sawdust."

IRON SPONGE FOR PURIFYING STEEL WORKS GAS.

Gas purification from the standpoint of the steel trade involves the question, Can the H_2S be removed from producer gas at a low cost? This can be answered in the affirmative without hesitation as the operation is taking place daily at every illuminating gas plant in the country, and those in charge will tell you that sulphur purification is the lowest cost on the list, ranging from 0.001c. to 0.002c. per 1,000 cu. ft., depending on the sulphur content, methods, employed, etc.

The material is used in the form of iron sponge, representing a mixture of the oxide with shavings, corn cobs, coke breeze or anything of like character. I would say, however, that shavings are generally employed, due to the ease with which they can be obtained as a rule and their cheapness. Coke breeze, which is usually present around an iron and steel plant, would answer the purpose just as well and there is no reason why it could not be employed successfully. Purifying boxes are built by a number of companies, and are comparatively inexpensive, simply representing containers for the oxide.

Until recent years the usual installation consisted of four cast iron boxes, rectangular in form and varying from 3 to 6 ft. in depth. In some cases they were elevated from the ground to permit of their being emptied quickly through openings in the bottom, and at the minimum expense. Usually, however, they were placed on the ground level, being filled and emptied by removing the covers. The boxes were generally housed in, to protect them from variations in temperature and to keep the operation of handling the oxide under cover. Recent practice has veered toward exposed steel cylindrical purifiers, which can be erected at a much lower cost than the old type of equipment. In some instances, they are elevated to reduce labor charges in emptying, but the preference appears to be for boxes placed on the ground, which are dumped and filled through doors or openings in the sides.

As a matter of precaution, exposed purifiers are often lagged with brick on the outside, sometimes on the inside, to guard against sudden changes in temperature; but this is largely a matter of location. The modern type of purifier is 10 or 12 ft. in depth and carries two and sometimes three layers, as compared with one, or two at the outside, in the older boxes.

THE METHOD OF PURIFYING.

The method of operation is exceedingly simple, when efficient purifying material is used. As a practical illustration, we will select a plant making 1,000,000 cu. ft. per day of water gas, containing approximately 100 gr. H_2S per 100 cu. ft., and purifying with four boxes holding 1,000 bushels apiece of iron borings oxide. It is claimed that half this quantity of the precipitated oxide would give the same or even better results, due to its unusual absorbing properties and high state of activity, permitting of a shorter reaction between the H_2S and the oxide than is required with iron borings oxide or natural ore.

The gas cooled down to 90° F., plus 1 per cent of air, which is added in various ways, is passed through the four boxes in turn, and then to the holder. At the termination of a week or ten days, the boxes are rotated; that is, No. 1, called the dirty box, is placed in the position of No. 3 or No. 4, depending on the method followed. If the latter, the position of the boxes after the first rotation would be 2, 3, 4, 1; following this, 3, 4, 1, 2; succeeded by 4, 1, 2, 3, and finally a return to their original position of 1, 2, 3, 4.

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*From The Iron Age.

†E. J. Lavino & Co., Philadelphia.

What is happening in the meantime? The greater part of the sulphur is removed in the first box; say, an average of 70 to 80 grains. With ordinary oxide the larger part of that remaining is removed in the second box and the final grains in the third box. The reaction involved in removing the H_2S is as follows:

$$Fe_2O_3{\cdot}H_2O + 3H_2S = Fe_2S_3 + 4H_2O.$$

But, besides this reaction, the following also occurs:

$$Fe_2O_3{\cdot}H_2O + 3H_2S = 2FeS + S + 4H_2O.$$

For some reason the oxide will not take up the oxygen in the gas, in the presence of appreciable amounts of H_2S. This explains why the dirty box is placed last; the H_2S having been removed in the first three boxes, the oxide is not hampered in taking up the oxygen and we have:

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 3S_2.$$
$$12FeS + 9O_2 = 6Fe_2O_3 + 6S_2.$$

In days gone by, before the use of air and the rotation system, it was necessary to dump or empty the first box, as soon as a stain appeared on the outlet of the second or third box, depending on the method followed. This meant frequent changes and high labor charges. With the rotation system and precipitated oxide, it should be possible to retain the oxide in place until it is completely fouled, depending on the question of back pressure.

If necessary to empty a box before it has reached the limit of its absorbing properties, the material is piled in a heap for a short time to heat up and then spread out in piles, so that air comes in contact with each particle of oxide.

CURRENT PRACTICE.

As absorption of 60 per cent, based on the total weight of the fouled mass, is considered to be the limit in efficient management, it may be possible to introduce more sulphur, but as this element increases the material becomes sluggish, and it simmers down to a matter of labor charges versus the additional quantity of gas old oxide will purify.

Mixtures of various strength are prepared. The writer knows of one gas plant using as small a quantity as 12.5 lb. of iron (not oxidized iron) per bushel. I am acquainted with another plant using 25 lb. of iron per bushel. When borings are employed, the usual mixture is 18 to 20 lb. of iron per bushel. This gives a product containing approximately 22 to 24 lb. of oxidized iron per finished struck bushel. Occasionally references are made to a heaping bushel, but as a rule the term bushel, as applied to oxide, represents a struck bushel of 2150.4 cu. in.

Oxidation in a short period is not a simple task, and if too much iron is employed, more or less of it never will become oxidized. By the time the material has been in use long enough to become completely transferred into oxidized iron, there is sufficient tar and oil present to prevent any further oxidation.

The recommended amount of oxide is 22 lb. per bushel, although as high as 35 lb. is employed by some works. The amount that can be employed to the best advantage is governed by the matters of tar and back pressure. If the gas is thoroughly cleaned before it reaches the purifying boxes naturally better results can be obtained with a 30 or 35-lb. mixture than with 22 lb. On the other hand, if the gas contains a small percentage of tar and oil, aside from rapidly reducing the life of the oxide, it leads up to back pressure and it becomes necessary to empty a box whether the material is still capable of removing sulphur or not.

A bushel of sponge containing 22 lbs. of precipitated oxide per bushel will purify from 150,000 to 200,000 cu. ft. of water gas (containing 100 grains of H_2S per 100 cu. ft.) and a proportionate quantity of coal gas. The exact quantity purified becomes a matter of purifying facilities, sulphur content of the gas, the percentage of tar and oil present, how the material is handled, and so forth.

Some plants fill their purifiers, and figuratively, if not literally, shut the doors of their purifier house and proceed to forget the operation. On the other hand, the average gas plant is purifying carefully, and delivering gas entirely free from hydrogen sulphide, with the minimum of trouble and at small expense.

The elimination of this element, while perhaps a new problem, so far as producer gas is concerned, offers no insurmountable obstacles, and any plant wishing to look into the matter can secure all the information needed to pass judgment on the merits of the case, without trouble or expense, by applying to the proper authorities.

Quinine exports from the United Kingdom totaled 485,006 ounces during the first three months of 1915, compared with 353,514 ounces and 328,108 ounces, respectively, in the first quarters of 1914 and 1913.

The total production of copper in 1914 was about 10 per cent less than that of 1913, according to statistics just compiled by H. R. Merton & Co., metal merchants of London. However, Germany's output increased during 1914 by 20 per cent and Austria's by 6 per cent. Since the beginning of 1915 there has been a general and steady increase of production owing to the heavy demands by belligerent countries, which presumably have caused the present high prices. The average price of standard copper in 1913, based on the figures of the 1st of each month, was £68 5s 9d, or $332.32 per ton; in 1914 the figure was £59 8s 11d, or $289.29 per ton; while the price on April 15,915, was £74 10s, or $362.55 per ton.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

The Canadian Forest Products Laboratories.

The Forest Products Laboratories of Canada, according to a paper read recently before the Canadian Section of the Society of Chemical Industry, intend to provide special facilities for study in the field of pulp and paper. To this end a separate building is being equipped to allow the carrying on of pulp and papermaking processes on a semi-commercial scale. The equipment, which will be installed in the near future, includes a very complete fourdrinier paper machine, which is the largest experimental paper machine ever constructed, single and double beaters with interchangeable basalt lava and steel rolls, small jordan engine, stuff chests, screens, paper testing instruments, etc. These will be followed by sulphite and sulphate digesters, bleaching apparatus, and such other equipment as is necessary to conduct experiments in a thoroughly practical manner. The pulp and paper industry is taking a keen interest in this development, and valuable gifts have been presented by various companies. One of the first investigations will be a study of the beating of paper pulp, which will include a comparison of steel and stone rolls.

Assistance in Relieving Dyestuffs Shortage.

The complete cessation in imports of chemicals, and especially of artificial dyestuffs, of German origin threatens to be a cause of widespread disturbance to nearly all American textile branches and to many other lines of industry. Managers of works in every section of the country are struggling to adjust themselves to conditions that call in many instances for a complete revolution in processes of manufacture and in the character of output, with resultant dislocation in all relations with consumers.

The few domestic color factories are putting forth every effort to supply in part the lacking dyes. Capital is also being embarked in new undertakings, designed to produce some of the simpler staple coal-tar colors, for which there is a heavy demand.

In the midst of this hurried readjustment by manufacturing interests, textile and other, to meet the exigencies of what threatens to be a temporary "dyestuff famine," and the equally hurried effort to replace foreign dyes by American-made dyes, it is the desire of the Bureau of Foreign and Domestic Commerce to lessen in every way feasible the severe strain to which all parties concerned are so suddenly subjected.

The bureau requests, therefore, that all consumers, in quantity, of foreign dyestuffs and chemicals in general, communicate promptly in detail the character and extent of their needs. Domestic manufacturers of dyestuffs, and newly started undertakings to place upon the market dyestuffs, coal-tar crudes and intermediates, and chemicals in general, are likewise requested to supply information as to just what products they are able to supply.

A clearing house for the mutual exchange of information between productive and consuming factors in this somewhat critical emergency, where time is an important element, is evidently needed. The Bureau of Foreign and Domestic Commerce will gladly fulfill this function.

Russian Rubber Industry.

The embargo on the exportation of rubber tires and rubber waste, exports of both of which had reached a considerable figure during the last few years, and, on the other hand, the considerable limitation of the demand both for industrial purposes and for the requirements of the population, have created a difficult position for the rubber industry in Russia. The manufacturing concerns that are obliged to continue the production of rubber goods are suffering from the scarcity of the necessary chemical supplies, as oxide of lead, etc. Oxide of lead was produced in Riga, but the concern was closed. A shipment purchased abroad was brought as far as Archangel, where it remains. The same happened to a consignment of rubber. Those interested are now organizing the importation of rubber through the port of Vladivostok, which, of course, will increase the price considerably.

According to a statement presented to the Ministry of Trade and Industry, the cost of rubber in Russia has increased 100 per cent. Besides, this industry is laboring under the absence of foreign currency for making purchases of rubber in England and from the insufficient supply of coal from the Donetz mining district.

The retail sales of rubber goods have greatly decreased. The retail dealers buy for cash only for immediate requirements. The price of all goods, rubber for technical purposes as well as goloshes, has advanced by 20 to 25 per cent.

Exports of rubber waste from European Russia amounted to $405,000 in 1912, $232,000 in 1913, and $73,000 in 1914.

Rewards for Methods of Utilizing Alcohol.

The U. S. Consul General John H. Snodgrass, Moscow, reports that in view of the limitation of the production of spirits at the present time and the importance of this industry to the agricultural interests the Ministry of Finance of Russia has found it advisable to take necessary measures to promote the industrial and technical utilization of spirits for technical requirements. To this end the Ministry has decided to establish an international competition with premiums for the best inventions in this respect. The total sum appropriated for premiums amounts to 265,000 rubles ($136,475).

The premiums to be awarded are as follows:

(1) A premium of 100,000 rubles ($51,150) will be awarded for the invention of a new method of utilizing alcohol for the manufacture of a product that will be essentially different from the alcohol used for its production. Examples of such products are vinegar, ether, chloroform, etc.

(2) A premium of 75,000 rubles ($38,625) will be awarded for the invention of a new method of utilizing alcohol for the manufacture of a product in which alcohol and its derivatives (sulphuric ether and others) form the component parts of the product or the solvent, and from which it will be impossible to extract alcohol with a view to profit (as, for instance, pharmaceutical preparations).

(3) A premium of 50,000 rubles ($25,750) will be awarded for the invention of a method in which alcohol and its derivatives would serve as a temporary intermediate solvent (as in the manufacture of smokeless powder and artificial silk).

(4) A premium of 25,000 rubles ($12,875) will be awarded for the increase of the heating value of alcohol by the addition of substances that will make the use of alcohol as fuel advantageous.

(5) Three premiums of 5,000 rubles ($2,575) each will be awarded for the invention or improvement of apparatus for the utilization of spirits in internal-combustion engines and for heating and illuminating purposes.

Inventions must be presented by Jan. 1, 1916. They must be presented to the Chief Administration of Taxes and Sale of Drinks, written in French or Russian, in special envelopes bearing some motto. In another envelope, bearing the same motto, must be stated the name and address of the sender.

The papers must contain a detailed description of the conditions of the adaptation of alcohol, indicating the cost of the method when calculating the price of alcohol at 2 kopecks (1 cent) per degree on the alcoholometer.

Premiums will be awarded only such inventions or improvements as will involve a considerable consumption of alcohol.

Antimony Smelting and Resources in Mexico.

U. S. Consul Wilbert L. Bonney, San Luis Potosi, reports that an antimony smelter is in course of erection in the city of San Luis Potosi and will be ready to start operation when mining and transportation conditions permit the ore supply to be shipped and the product exported. The machinery, which is American, is now ready for installation. It is expected that the plant will employ 150 men and the capacity is to be 3,000 tons per annum of refined star antimony. The product will be shipped to the United States. This will be the first and only smelter in Mexico producing refined antimony for the market. It is owned by American capital and will draw ores from its own properties in San Luis Potosi and Queretaro.

The only antimony smelter heretofore operating in Mexico is located at Wadley, a small station on the National Railway, 102 miles north of San Luis Potosi. The Wadley smelter is not equipped for finishing the product, and has exported its product to England for further refining. The Wadley plant was erected about 14 years ago, and has drawn a large part of its ore from the Catorce district.

Antimony has been found in many places in Mexico, especially in Durango, Sonora, and Oaxaca, and relatively small amounts of ore have been shipped to the United States for smelting; however, the Catorce deposits have been the best producers for the last 20 years. The mining ores run from 25 to 70 per cent pure antimony. Antimony appears in many ores treated at the lead smelter in San Luis Potosi, but its presence in these ores is deleterious, and in the bullion it is regarded as an impurity.

POSITION WANTED as assistant chemist. Completed the I. C. S. General Chemistry Course and the manufacture of sulphur and hydrochloric acid. Married. Have a responsible position in another line of work; desire a change. Box 6, Chemical Engineer, Chicago, Ill.

CHEMIST, also electrical engineer, desires position as chemist with a reliable company, with opportunity for advancement. Excellent references and a wide experience as analyst. Age 26. Address M., care Chemical Engineer, Chicago, Ill.

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INDUSTRIAL RESOURCES OF THE SOUTH.*

By ARTHUR D. LITTLE.†

Only those who have stood upon the seashore and there endeavored conscientiously to place the Atlantic Ocean inside a quart bottle by the aid of a teaspoon will appreciate the temerity and difficulties involved in an attempt to present within the compass of a brief address the industrial potentialities of the South. Probably no one but a relative stranger to the South would make the attempt at all. Nevertheless we are all prone to overlook the obvious in our immediate surroundings, and the visitor who looks upon them from a different standpoint with sympathetic interest and keen appreciation may sometimes point out new aspects in them and values before unrecognized. The man who views a mountain range from a distance may even trace its outlines and sense its trend better than those who dwell upon its slopes. So it happens that one whose knowledge of the South is in no way comparable to your own may hope, through your indulgence, to enlist your interest and possibly to turn your thought in new directions.

The awful spectacle of a world in arms which we are forced to contemplate today must recall with a peculiar vividness to many men and women North and South the horrors and desolation of another struggle which was concluded, happily as we all now believe, just fifty years ago. When we consider that the wealth of the whole United States in 1850 was estimated at a little more than $7,000,000,000, and the cost of the war to the South has been conservatively figured at $4,000,000,000, we may gain some faint notion of the material burden under which the South slowly arose to work out her destiny.

The situation she then faced was one to daunt the stoutest hearts. It involved a reorganization of the whole economic and social structure in a land mourning the loss of the flower of its youth and manhood, with broken credit, capital destroyed, industry prostrate, and streams of immigration diverted. To the burdens of the Reconstruction Period were added the paralyzing fallacies of the Greenback issue and the nationwide disasters and stagnation of the panic of 1873 and the five lean years which followed. Not until 1880 did the South begin to come into its own.

Extent of Southern Industries.—In 1880 the agricultural capital of the South was $2,762,000,000 and the total value of its agricultural output $756,000,000. The cotton crop was 5,761,000 bales, of which the South used 179,000 bales and the North 1,610,000. Only about $330,000,000 were invested in manufactures; the mineral output was $18,000,000; the railway mileage was approximately 25,000, and the population 18,600,000. With these figures in our minds let us attempt the construction of a concept of the industrial South today.

The population of the South in 1912 had risen to 33,475,000, and the railway mileage to 90,930. The population of the whole United States in 1880 was about 50,000,000 and the total railway mileage 93,000. In general it may be said that the South today is in a far stronger position industrially than was the entire country in 1880. It cuts more lumber, mines nearly twice as much coal, produces nearly four times the petroleum, and nearly six times the spelter. It has more looms and spindles and a much larger investment in manufacturing plants. Its agricultural capital is greater and the products of its farms are worth 50 percent more. It makes nearly as much pig iron and twice as much coke as the whole country produced only thirty-five years ago.

Agriculture in the South.—Agriculture is still and always will be the greatest business of the South and the backbone of its prosperity although even now the value of manufactured products exceeds, by nearly $900,000,000, the revenue from its farms.

As all the world knows, the South affords a peculiarly favorable habitat to the cotton plant and the 36,000,000 acres under cotton produce annually from 14,000,000 to 16,000,000 bales of the fiber, or about 65 percent of the world's crop. In this connection it may be said in passing that chemists by developing methods for utilizing values in the cottonseed have added from $12 to $14 per bale, or perhaps $200,000,000 yearly, to the value of this single crop, so that the seed alone is now worth nearly as much as the entire crop of 1860. Cotton and seed together constitute about 30 percent of the total value of southern farm products, excluding live stock. The ultimate products of the cotton plant constitute 30 percent of the merchandise exports of the whole United States. The value of staple, linters and seed in 1913 was $911,000,000. Corresponding values for 1914 were $704,000,000, so that the European war may fairly be said to have cost the South, on this one item, over $200,000,000.

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*From the Journal of Industrial and Engineering Chemistry. Opening address at the New Orleans meeting of the American Chemical Society, March 31 to April 3, 1915.

†Ex-President of the American Chemical Society; Former Official Chemist of the American Paper and Pulp Association.

Many years ago a certain cafe in New York attained a cheap but widespread notoriety by embedding in the mosaic of its floor a few hundred silver dollars. There are 600,000,000 acres in the South and nearly every one of them carries on its surface more dollars than the floor of that cafe. Upon 110,000,000 of these acres the South now raises crops valued at more than $3,000,000,000. From 1880 to 1910 agricultural capital increased from about $2,800,000,000 to nearly $11,000,000,000, or 296 percent.

In spite of the proud preeminence of cotton in southern agriculture a considerable diversity of crops has already been established. Texas alone has raised 200,000,000 bushels of corn in a single year and the value of the 1913 corn crop in the South was $766,000,000. In that year the value of the hay raised was $111,000,000, wheat $95,000,000, and tobacco $72,000,000, with another $125,000,000 in oats, Irish and sweet potatoes, sugar cane and citrus fruits. Twenty million head of cattle, 25,000,000 swine and 9,000,000 sheep add their value to the wealth of southern farms.

Manufacturing in the South.—Strangers to the South do not commonly think of this portion of our country as a manufacturing community. They may therefore well be surprised to learn that already the manufactures of the South greatly exceed in value the products of its farms and reach the stupendous total of more than $4,000,000,000. In the twenty-nine years from 1880 to 1909 the capital invested in the South in manufactures increased 900 percent and the value of manufactured products 407 percent. The census survey of the entire country enumerates 262 different lines of manufacture. Of these 236 are already carried on in the South. Sixty-five percent of the new spindles installed in the United States since 1890 are in place in southern cotton mills which now operate upward of 12,000,000 spindles and consume nearly 3,000,000 bales of cotton, whereas the northern mills in 1913 used only 2,500,000. Two southern States already manufacture more cotton than they raise. The value of cotton goods produced is nearly $250,000,000. One seldom hears of southern flour and grist mills, yet their product reaches the striking total of $209,000,000.

The factory products of one southern State, Missouri, reached a value of $1,688,000,000 in 1912, which included neaarly $50,000,000 in boots and shoes and corncob pipes to the number of 28,000,000; the value of Missouri manufactures today is probably nearly or quite equal to the total value of southern agricultural products in 1880. West Virginia claims the largest pottery and largest glass factory in this country and the largest ax factory in the world.

In nine years, beginning with 1900, eleven southern manufacturing industries, including some of the greatest importance, increased their annual output by amounts ranging from 259 percent to 2,380 percent. The total increase in ninety-two leading industries was from $1,288,000,000 to $2,696,000,000, or 106 percent. During the same period capital invested in factories rose in Texas from $64,000,000 to $217,000,000.

Southern Forests and Lumber Industries.—The total forest area of the South is estimated at 259,000,000 acres. That of Germany is about 35,000,000. In 1913 the whole United States cut 38,000,000,000 feet of lumber, of which the South cut more than 22,000,000,000, including fifteen billion feet of yellow pine. One Louisiana sawmill cuts 1,000,000 feet of this wood a day. Eight years ago the site selected for this mill was in a stretch of virgin forest. Today it stands upon the outskirts of the thriving and unusually attractive little city of Bogalusa with more than 10,000 inhabitants and stores, residences and public buildings which would be the pride of many an older community of much greater size.

The outstanding predominance of yellow pine should not cause us to overlook the fact that of more than fifty woods manufactured into lumber in the United States the South cuts upward of forty. In case of ten of the more important of these fifty woods the cut of individual southern States ranks first.

The annual value of southern lumber is about $350,000,000, but the reported cut excludes so many primary wood products of larger importance that at least another $100,000,000 must be added to represent their value and $25,000,000 more for naval stores.

Coal, Coke and Iron.—Coal lies at the basis of civilization and its stored up energy is the present measure of man's command over nature. Excluding lignite, the coal areas of the southern States amount to about 88,000 square miles or more than fifty times the coal areas of Germany, seven times those of Great Britain and twice those of all Europe, including Russia. The South's present proved reserves of coal are estimated at 530,000,000,000 tons, or 25 percent more than the more thorough exploitation of all European countries as disclosed—and these southern reserves comprise 75 per cent of all the coking coal in the United States. West Virginia alone has a far greater coal area than Great Britain and Germany combined and she has mined less than one-sixth of 1 percent of the 150,000,000,000 tons beneath her surface. Nevertheless her 1912 output of 67,000,000 tons was 50 percent more than all the bituminous coal mined in the United States in 1880. Alabama already stands next to Pennsylvania in coke production.

With coal, limestone and iron ore closely adjacent within her borders, Alabama has already demonstrated her ability to manufacture pig iron more cheaply than any other locality on earth—and "he who has the iron will get the gold." Her present output of 2,000,000 tons is merely an earnest of her potentialities. The immediately available southern iron ores are estimated at 2,600,000,000 tons with even greater reserves of ores of lower grade. Together these constitute not less than 50 percent of the total iron ore reserves of the country.

Petroleum and Natural Gas.—It is doubtful if any American product is better known throughout the East than those tins of kerosene which bear the label of the Standard Oil Company. Our automobiles consume an amount of gasoline equivalent in volume to the water supply of a town of 40,000 inhabitants. The range of endeavor of Newfoundland fishermen is determined by its price and the flight of aeroplanes over the battlefields of Europe is measured by its supply. In 1890 the South produced less than 500,000 barrels of petroleum. In 1912 its output was 84,800,000 barrels. Passing by the great deposits of Louisiana and Texas, it may be pointed out that the oil production of Oklahoma alone in 1911 was 54,000,000 barrels.

Among those bounties of Nature with which the South has been so plenteously endowed few have greater potential values and none have been wasted more recklessly than natural gas. More than 60 percent of the gas output of the country, or 290,000,000,000 feet, must now be credited to the South. From the standpoint of industrial utilization this is more than 1,000,000,000 feet per working day.

Waterpower in the South.—The relative cheapness of waterpower as compared to steam has determined in the North the location and development of many great manufacturing centers like Holyoke, Lowell and Lawrence in Massachusetts, and Rumford Falls and Lewiston in Maine. The application of this power to electrochemical industries has made Niagara Falls the most interesting place on earth to chemists. Cheap waterpower not only implies but insures the ultimate development of public utilities and the establishment of manufacturing plants within the radius which it may serve.

Seven years ago the United State Geological Survey estimated the minimum available power in eleven of the streams which have their headwaters in the Southern Appalachian Mountains at 2,800,000 hp. The estimate for all the streams of the South has been put at about 5,000,000 hp. Only about one-fifth of this power has been developed and of this amount nearly 800,000 hp. is in the five States of Alabama, Georgia, North Carolina, South Carolina and Virginia. Georgia alone has available 500,000 hp.

Secondary Mineral Resources.—The lavishness with which Nature has bestowed her gifts upon the South is nowhere more apparent than in the extraordinary variety and range of what may be termed the secondary mineral resources of this fortunate section of our country. An output of $5,800 worth of diamonds per week of the best South African quality in Pike county, Arkansas, is interesting and promises to become spectacular, but it shrinks to insignificance before many other southern mineral products. The whole country knows of the annual shipment of 8,000,000 boxes of Florida oranges and grape fruit, but relatively few of us give thought to the 3,000,000 tons of the infinitely more important phosphate rock which Florida produces. This is about four-fifths of the country's output, practically all of which now comes from the South.

Portland cement requires for its manufacture an assured supply of limestone and clay or shale adjacent to cheap fuel. Nowhere are these conditions met more fully or more generally than in the South. As a result its development of the manufacture of Portland cement has become one of the industrial miracles of the world. In 1890 the production for the whole United States was less than 400,000 barrels. In 1911 the output of cement in the southern States alone was nearly 11,000,000 barrels.

The South has inexhaustible supplies of clays which exhibit every desirable range of quality. There are clays in any amount desired for the making of common brick and tiles, cheap pottery and drain pipe, terra cotta and paving brick, and prodigal amounts of the finer white plastic clays and kaolins for china and the purposes of papermaking. The production of fuller's earth is almost exclusively a southern industry.

The South is equally fortunate in its endless stores of sand and gravel, road material and building stones. The latter range from the superb Georgia marbles and the granite of Stone Mountain near Atlanta, through every variety and quality, to meet all structural demands.

Immense deposits of gypsum occur in several southern States and ochres, mica, graphite, barytes and corundum are among the well known mineral products of the South.

The history of industrial chemistry is a record replete with romance, and one of its best known stories is that which chronicles the development of the aluminum industry. In 1855 the metal cost $90 a pound; the Castner process brought the price to $4 in 1889. Then Hall in America and Héroult in Europe simultaneously developed the process which permits its cheap production by electrolyzing alumina in a fused bath of cryolite. Bauxite is an impure alumina and has become the chief source of the metal. Arkansas leads in the production of bauxite, but Georgia, Alabama and Tennessee contribute largely to the growing demands.

Another romance of chemical achievement is that which tells the story of the sulphur mines in Calcasieu Parish, Louisiana. There sulphur in inexhaustible amounts lies 1,000 feet below the surface and under 500 feet of quicksands. An Austrian company, a French company and many American companies had tried in many ingenious ways to work this deposit, but each had failed. Frasch solved the problem by forcing superheated water down a boring, and pumping out the melted sulphur through an inner tube. Today

Louisiana holds easily within her hands the sulphur markets of the world and supplies half the world's consumption.

Sulphur, as the direct source of sulphuric acid, constitutes the foundation of all chemical industries. The keystone of the structure is common salt. This the South bountifully supplies at Avery's Island, also in Louisiana, and in the salt wells of Oklahoma and West Virginia.

The largest sulphuric acid plant in the world is at Ducktown, Tenn., but the striking feature of the installation which holds this record is that the acid is made from smelter fume, which commonly in other plants goes only to create a nuisance. The copper production, which is the primary output of the plant, exceeds 18,000,000 lbs. a year. The largest copper refining plant in the world is at Patapsco, Md., with an annual production of 200,000,000 lbs.

In 1911, 42 percent of the lead output of the country came from the South and 41 per cent of the zinc production. The value of Missouri zinc alone was $14,000,000. The largest pyrites-producing plant in the whole country is in Louis county, Virginia.

There are produced in the United States fifty-seven useful minerals. Of these every one is mined in the South except platinum and borax.

The Failures of the South.—We have reviewed in the most casual and disjointed manner the immediate achievements and demonstrated resources of the South in those things which make for industrial preeminence. All these figures are well known to you. They have been set forth time and again in the publications of the Federal Government and those of your own States, and reiterated with compelling emphasis and illuminating comment by that apostle of southern achievement and prosperity, the *Manufacturer's Record*. The aggregate of these stupendous figures represents an achievement and a heritage of which any people may well be proud, but the community whose eyes are filled with a vision of the future should take measure not of its success but of its failures. What are the failures to be charged against the South?

First of all there is the stupendous failure of its agriculture. In 1909 only about 18 percent of the total area of the South was tilled, whereas 75 percent is available for tilled crops. What is more to the point, the 110,000,000 acres which were tilled were most of them tilled badly. Upon 35,000,000 acres the South raises as a maximum 16,000,000 bales of cotton—less than half a bale an acre. In some localities the yield shrinks even to 132 lbs. per acre. As compared with this, Georgia has raised upon 2,500 acres 2,700 bales, while as much as 2.38 bales has been raised upon a single acre in Texas. Little more than deeper plowing and intelligent fertilization is required to double the present crop or to produce the 1914 crop upon half the present acreage, leaving 18,000,000 acres available for corn and other crops. In one southern State 232 bushels of corn have been raised on a single acre; in another, thirteen acres of lettuce have sold for $12,000; and in a third, 5,000 acres of cabbages have yielded $800,000, and 2,000 acres $600,000 worth of cucumbers. In the same State 145 million cabbage plants were started upon 346 acres and exported to other States to complete their growth. A single acre of Florida celery has paid $1,500 in freight to the railroad. North Carolina, which shipped 1,600 carloads of strawberries from Wilmington in one season, reports 15,000,000 acres within the State upon which no agricultural improvements have been made. Alabama still buys largely of western grain, provisions and even hay, while Arkansas bought $80,000,000 worth of foodstuffs last year.

Next perhaps in importance is the failure of southern lumbering, which is one of the most wasteful operations conducted on the whole broad face of the earth. In cutting 15,000,000,000 feet of merchantable yellow pine the South wastes not less than 30,000,000,000 feet, which, if intelligently utilized as raw material, should yield ten times the profit derived from lumbering.

For every ton of coal mined in the South, or for that matter in the country, half a ton was wasted or left underground in such condition that it can probably never be recovered.

The most atrocious and unnecessary wastes which have attended the development of any resources of our country have been those which have accompanied the exploitation of natural gas. As to these the South is no more culpable than other portions of our country upon which this extraordinary boon of nature was conferred. Nevertheless it may interest you as southern men who would conserve the resources of your birthright to know that the waste of gas in the Oklahoma fields alone has been as high as 150,000,000,000 cubic feet a year, and is now annually not less than 25,000,000,000 cubic feet. The time is fast approaching when natural gas will have its value determined by the number and value of the synthetic products which chemists are able to derive from its several components. For the present it may suffice to point out that every 100,000,000 cubic feet of natural gas represents on the basis of a ten-hour day 588,000 horsepower, if consumed in a fair gas engine on fluctuating load averaging 50 percent of rated capacity. West Virginia is now the largest producer of natural gas in the country and the especial disability under which the South now labors is exemplified by the fact that a very large part if not the major portion of the gas originating in West Virginia is piped outside the State and used for the generation of heat and light and power elsewhere.

It has already been pointed out that the South contains upward of 50 percent of the total iron resources of the country. Nevertheless it produces only 12.5 percent of the pig iron made and consumes not more than 150 lbs. per capita, while the whole country consumes 650 lbs. per capita. Here again we have before us the fundamental difficulty which confronts the

South. A ton of iron ore shipped as ore returns only $2 and provides less than one day's work for one man. If shipped as stoves it returns $40 and has provided a day's work for ten men. The South has been selling raw materials. It should sell brain values and labor values.

Owing to its later advent as a large producer and its relatively more general introduction of by-products from coke ovens, the South has been less wasteful than the North of the ammonia values in its coal. It will probably never be possible to recover more than a moderate proportion of these values, but the extent of the problem in the whole country may be indicated by the fact that the total volatile ammonia in the coal mined annually in the United States would be worth, at $60 per ton for ammonia sulphate, upward of $300,000,000. We save less than $4,000,000. In Germany four-fifths of all coke is made in by-product ovens; in the United States only about one-sixth is so made.

In the Florida pebble field the tonnage of phosphate rock wasted is two or three times the total tonnage saved. The waste occurs mainly through the washing away of fine particles by the water used in mining and for cleaning the larger aggregates. In the Tennessee field there is relatively much less waste.

The wastes in zinc mining and smelting constitute another heavy drain upon your resources. Less than 50 percent of the zinc in the mines ever reaches the form of spelter.

Many other comparable examples of the prodigal use of utter waste of valuable raw material might easily be cited though perhaps to no advantage at this time. There are signs that the era of thoughtless or willful extravagance is passing. Means of production, methods of practice and systems of organization which have been worked out painfully and at great cost elsewhere are being gradually adopted in the South but a more general appreciation of their advantages may well be urged.

The Pulp Mills at Canton, N. C.—An excellent example of intelligent conservation is afforded by the great pulp mill at Canton, N. C. Formerly the spent chips from the chestnut extract plants were burned. Now they are boiled in caustic soda and converted into high grade pulp and paper.

All visitors to the South who have been so fortunate as to partake of the hospitality of southern homes cherish always thereafter a warm appreciation of the grace and courtesy of southern life. The charm of New Orleans is proverbial and the metropolitan aspect and quality of many southern cities like Jacksonville and Atlanta strikes the observer at once. One may nevertheless be permitted to suggest that the South would gain immeasurably by giving to a larger proportion of its smaller towns and country places that atmosphere of trig neatness and comfortable prosperity which characterizes so many of the older villages of Massachusetts and Vermont and reflects the pleasantness of life in them. The South is also greatly handicapped by the general quality of its roads. Only about 60,000 miles out of 850,000 have ever been improved.

Value of Industrial Training for Negroes.—One of the greatest of the relatively undeveloped potential industrial assets of the South is undoubtedly the Negro. The Negro population in the southern States is about 10,000,000, and by the efficiency of the units of that population the prosperity of the South is profoundly affected. Many Negro farmers are now raising from 30 to 60 bushels of corn per acre where formerly they raised from 5 to 15 bushels. Where they produced from 150 lbs. to 250 lbs. of lint cotton per acre many now secure 250 lbs. to 600 lbs. Nevertheless, a demonstration agent of the Department of Agriculture has recently found Negroes farming almost entirely by hand. Three persons carried on the planting of the grain: the first would dig a hole for the seed, the second would plant it and the third would cover it. He introduced the use of the plow in this twentieth century.

Scarcely any work carried on in the South today is more truly constructive or fraught with greater ultimate possibilities than that which goes forward at Tuskegee and in those other institutions of which it is the type. Since its foundation approximately 9,000 young Negro men and women have received two years of industrial training. They entered with an average earning capacity of about $100 per year. Their earnings after training have averaged $700, which by the way is above the average for doctors and lawyers in Massachusetts. The average length of time that these 9,000 students have been out is fourteen years and in that time their estimated earnings have been $88,200,000. Deduct from this the $12,600,000 which they might have earned without their special training and the already accrued value of that training which it cost Tuskegee $1,467,000 to impart is $75,600.000. Is there any more profitable business in which the South can engage?

We have given a brief consideration to the imperial resources of the potential South and have sketched in a few high lights, in an attempt to picture something of the South's amazing progress and achievement. Let us turn our attention to the trend and goal of her development.

Southern Rural Life Needs Enrichening.—The first of her problems would seem to be the organization of rural life to make it richer, more satisfying, more profitable and pleasanter. It is bound up with the problem of the reorganization of southern agriculture. The South has really not begun to farm. To prove this thesis one has only to turn to the results secured by agricultural demonstrations, demonstration farms, boys' clubs, the girls' tomato clubs, the McRae experiment in North Carolina and the output of truck farms under scientific control in many southern States. There is not a single southern crop which cannot easily be increased 500 percent. For 2 percent of the value of a single potential crop 20,000,000 acres of swamp land in Louisiana could be drained and the South's output of cotton doubled. There are no more fertile lands on earth than the Louisiana lowlands, and Louisiana, which might have been in ages past another Egypt, should become another and a greater Holland, and in Holland lands potentially less productive sell for $500 to $1,500 per acre. Tennessee has a swamp area of 1,000,000 acres. Along the Atlantic Coast are 25,000,000 acres of sandy loam ideally adapted to intensive farming. Texas has an area of 170,000,000 acres, greater by 55,000 square miles than either France or Germany, but less than 30,000,000 acres are yet improved. It now carries over 10,000,000 head of live stock, while Texas bees are worth $5,000,000 and produce each year honey and comb to the value of $5,000,000. It pays to keep a bee in Texas.

One yields in passing to the temptation to refer to the camphor trees of Florida and Texas and the date palms profitably grown on the islands near the Texas coast. But details and figures merely obscure the broad and basic proposition which is that the agricultural possibilities of the South are almost beyond conception and that in their development can profitably be employed all that enterprise, capital and science can supply for many years. Diversified, intensive agriculture by individual endeavor, corporation farming and community effort under scientific direction and control will find full scope and reap harvests unthought of now.

Conservation—the Foremost Industrial Problem.—Foremost among the industrial problems of the South would seem to be the suppression of wastes, the vastly greater development of labor values in its products and the keeping at home of money now needlessly spent elsewhere. The South has been too generally content with shipping crude materials and primary products and too ready to accept from other sections the things which it might better produce at home.

For gigantic wastes which may immediately be utilized to the enormous profit of the South, no industry is comparable to the lumbering of yellow pine. Our studies have shown that in Louisiana at least, under exceptionally able management, the products of the average yellow pine tree may be classified as follows: Needles and twigs, 2.25 percent; limbs under 3 in., 2.54 percent; cordwood, 6.142 percent; pulpwood, 4.154 percent; red and rotten, 8.05 percent; sawdust and shavings, 17.62 percent; lightwood, 0.61 percent; stump, 6.48 percent; lath, 1.39 percent; shingles, 0.06 percent; and finally lumber and box shooks, 31.97 percent.

Two-thirds of the tree is at present wasted either as litter in the field or as mill waste; and $3 a thousand is a good profit on lumber.

Opportunities for Papermaking.—While northern paper mills are paying on the average $18.37 for the wood to make a ton of paper the South is throwing away tens of thousands of cords of pulpwood every day, only a cord and a half of which is needed to make a ton of kraft paper worth $70. The ultimate development of a vast paper industry in the South is assured, but as a recent editorial in the New Orleans *Item* pointed out, "Great industries do not spring from great opportunities. They result from the initiative of some individual. The captain of industry may create an industrial empire in a desert and bring his material hundreds of miles from spots far more favored by nature than is their destination. We in Louisiana lack industrial empire because we lack captains of industry."

The recently culminating discoveries in a century long research have proved that 20 gallons of 95 percent ethyl alcohol—that is, not wood alcohol, but the alcohol commonly produced from grain—may be obtained from a cord of yellow pine sawdust or hogged waste. From a bushel of corn worth, say, 80 cents, only 2¼ gallons are obtained. Such difficulties as have attended the initial large scale operation of this process are certain to be overcome, and have in fact for the most part already been surmounted. Cheap industrial alcohol made in enormous volume from yellow pine waste and available for motor fuel, lighting, heating and a thousand miscellaneous applications in the arts is a certainty of the future.

In Georgia a great plant for the production of naval stores is shut down, primarily, it is said, because the annual loss of solvent represented 23 percent of the entire plant investment. New processes promise a solvent loss of less than 2 percent.

Several types of gas producer are now operating profitably on wood waste. New methods of controlled distillation have been developed and applied to wood and it has been proved both by the Forest Service and our own laboratory that turpentine and rosin may be profitably extracted from stumps and lightwood by processes which permit the manufacture of paper from the extracted chips. The production of lumber in the South will ultimately become a mere incident in the business of lumbering. No longer then will logging tramways be pulled up the moment the saw logs on the tract have been removed. They will stay until the tract is cleared of cordwood, pulpwood, lightwood, stumps and saw logs. The cleared land will be devoted to grazing or to farming under the stimulus of demonstration farms or corporation management, and the lumber mill will become the center of a whole group of highly profitable industrial activities.

Present Manufacturing Limited.—Less than 30 percent of the lumber produced in any southern State receives any further handling in the State of origin. Cottonseed oil is shipped to Chicago, Berlin and New Hampshire, to be hydrogenated and converted into lard and butter substitutes. Bauxite is sold for $5 a ton to be subjected elsewhere to the purifying treatment which raises its value to $60. The South will one day benefit enormously by a cheap process of producing alumina direct from clay. It will give new values to southern clay beds and to southern waterpowers and transfer the aluminum industry to this section. It does not appear, however, that any effort is being made in the southern States to develop such a process.

There are at Webster, N. C., millions of tons of low-grade nickel ore awaiting only a commercial method of extraction. Thus halloysite in large quantities occurs on Taylor's Mountain, near Gore, Ga. It contains 30 to 35 percent of alumina, said to be soluble in dilute sulphuric acid to form a clean white alum cake almost wholly free from iron and silica. If these claims can be established there is the basis for a large industry. A single northern paper company consumes 12,000,000 lbs. of alum a year.

No locality in the United States and perhaps none in the world presents such advantages for the establishment of the great basic chemical industries as Louisiana. Here in close juxtaposition are found cheap salt, even cheaper sulphur, gas, oil, rosin, turpentine and wood waste, while near by are the coal and minerals of Arkansas and Alabama.

Small Number of Chemists in the South.—It is noteworthy, in view of the extraordinary opportunities for chemical development presented by the South, that in the southern States are to be found only about 10 percent of the chemists of the country as represented by the membership of the American Chemical Society. The society has 7,180 members, of whom only 746 are in the entire South, whereas New York has 1,186 members, Pennsylvania 659, Massachusetts 511. What one chemist can do for the South has been shown by Frasch in Louisiana, by Wesson wherever cottonseed oil is made, and by our distinguished president, Dr. Herty, in the conservation of turpentine and increase of yields.

TSINGTAU SOAP FACTORY.

The *Far Eastern Review* states that a Germaan chemist recently erected a soap-manufacturing plant in Tsingtau, China, which appears to be having considerable success. The idea is to manufacture toilet and washing soaps to be supplied to the natives at lower prices than the imported products. The factory, which is equipped with machinery from Germany, is run entirely by electricity and has Chinese employes. It is said that pure fat only is used in the manufacture of the soaps, and the toilet soaps are claimed to be much superior to the imported soaps that can be purchased at anywhere near the same price. The soap is clean, mild, soft, and gives a strong foam in washing, with a delicate perfume, and will stand comparison with much more expensive imported products.

A novelty that has been introduced is the sale of soft soap in 22-pound graniteware buckets that, complete with wooden cover, sell for $3.80 Mexican ($1.79 gold), an 11-pound bucket of soap selling for $2.20 Mexican ($1.03 gold). The cost of the bucket and soap together is less than the price of the buckets alone in the regular retail shops of the city.

CHEMISTRY IN THE DEVELOPMENT AND OPERATION OF FLAMING ARC CARBONS.[*]

By WILLIAM C. MOORE.[†]

In an arc struck between two carbon electrodes, very nearly all the light comes from the incandescent electrode tips. In a direct-current arc, the positive crater is larger, and possibly at a higher temperature than the negative crater, and it is this positive crater which is the source of most of the light. Since the crater is merely an incandescent solid, it affords a continuous spectrum; colorimetric experiments recently made by L. A. Jones, and reported by him at the Cleveland meeting of the Illuminating Engineering Society, September 1914,[1] show that this incandescent crater has about 67 per cent of the daylight value of noonday sunlight. When volt-ampere readings are taken with such an arc, it is found that if the arc is lengthened, the voltage rises and the amperage falls, and eventually the arc goes out. If, as in the present instance, we use as one of our electrodes a carbon rod which has been hollowed out into a cup, and place in the cup some potassium chloride, and again strike the arc, we find that the volt-ampere characteristics are changed and that at the same amperage, a much longer arc can be drawn. Cassellmann in 1844[2] seems to have been the first to have noticed this fact. As we see, an arc fed with potassium chloride gives very little light; in fact, probably less than the pure carbon arc as the positive crater is not so bright. This arc has a distinctive color, and, of course, would show beside the carbon arc lines, the potassium lines in the spectroscope. Bunsen[3] in 1844, seems to have been the first to notice that different materials give different spectra in the arc.

If, instead of potassium chloride, we place a small amount of calcium fluoride in the hollow carbon cup, which, in this as in the previous case, is in the lower positive carbon, we find that the arc length for a given current and voltage is much shorter than for potassium chloride, and longer than for a pure carbon arc, moreover, the arc is intensely luminous, though rather unsteady and liable to go out. On placing a mixture of potassium chloride and calcium fluoride in the arc, we get the combined advantages of a long arc, with more intense luminosity than is afforded by either the pure carbon arc or the potassium chloride arc alone. These simple facts form the starting point in the development of the modern flaming arc. About 1899, Bremer, in Germany, brought out a flaming carbon, with calcium fluoride as the essential light-giving salt. The light afforded by such a carbon is a sensation yellow; the color is more aptly described however, as "minus blue," as the spectrum of such an arc is very deficient in the blue.

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[*] Paper presented at a meeting of the New York Section, Nov. 10, 1914, in joint session with the American Gas Institute and the Illuminating Engineering Society, and called up for discussion at the 27th General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22-24, 1915.

[†] Research Laboratory National Carbon Co., Cleveland, O.

[1] Trans. Illum. Eng. Soc., 9, 687 (1914).

[2] Pogg. Ann., 63, 576 (1844).

[3] Berzilius, Jahresbericht über die Fortschritte der Chemie und Mineral, 25, 20 (1845).

From 1899 to the present, the development of the flaming arc has been going on steadily and surely. It is interesting to note that the first record the National Carbon Company has of any work being done by them on the subject was when some ordinary cored carbons flamed and experiments were undertaken to prevent this phenomenon.

Although Bremer produced a carbon which could be burned vertically, for a number of years most of the commercial lamps were "inclined trim" lamps taking long, cored carbons, which burned under open-arc conditions. A few years ago, however, there was developed a lamp for burning flame carbons in a vertical position, and for these lamps solid carbons have been developed. An interesting point is that the idea of solid carbons antedated the development of the lamps. These lamps generally operate in such a way that a limited supply of air reaches the arc, that is, under "enclosed-arc" conditions. These various types of lamps are doubtless familiar to the illuminating engineers present.

Modern flame carbons may be classified in several ways. From the standpoint of the mechanical structure of the finished carbon, we have cored carbons and solid carbons. From the standpoint of the color of the light emitted by the carbons, we have a major division in which are included yellow flame carbons and white flame carbons, and a minor division including red, green and blue flame carbons, red and green being but little used except for advertising purposes, and blue being used as a source of blue and ultra violet light for medicinal purposes.

In the major division, calcium fluoride is the chief constituent of yellow flamers, and rare earth compounds the chief constituents of white flamers.

A brief description of the method of manufacture of flame carbons may not be out of place. The first step, of course, is the careful weighing out of the requisite amount of the carbon base, and the proper flame materials for making a "mix." Most of these mixes are rather complex. After weighing, the ingredients are very thoroughly incorporated together and with an appropriate binder—generally tar, or pitch, or a mixture of these. The "mix" is then forced by means of a hydraulic press, into long rods, which after cooling are cut into the proper lengths. These green carbons are then carefully baked in gas-fired furnaces and the temperature gradually raised according to a definite schedule, the final temperature attained being determined by a number of factors, such as the liability of some of the constituents to volatilize, or to react with each other and the carbon.

After cooling the furnace, the carbons are unpacked, sorted, cleaned and gauged, the latter process consisting in determining the diameter, as but small variations in diameter are permissible; the carbons must also be quite straight. Some solid carbons are electroplated with copper on the holder end to make a better contact between the lamp holder and the carbon. After plating they are dried and made ready for shipment. It is, of course, necessary to keep all flame carbons dry, as water may cause reactions between some of the flame materials, or may set up a carbon-copper cell with some of the soluble or partially soluble salts as electrolytes and thereby destroy the copper coating. Water has another detrimental effect as shown by W. R. Mott,[4] namely to react with the carbon at high temperatures, forming carbon monoxide and hydrogen; the latter may not only accumulate in the lamp housing and cause the lamp to explode when started again, but rapidly conducts heat away from the burning arc and lowers its efficiency.

The manufacture of cored carbons is quite similar to that of solid, except that the carbon base is different, and in forcing the die contains a pin which makes the carbons hollow. After baking, sorting and gauging this core hole is filled with a mixture of a carbon base and the flame materials with an appropriate binder, and the carbons are then dried. As cored carbons are usually very long and of small diameter, a zinc wire is inserted into a small hole parallel to the core hole. This wire increases the conductivity of the carbon. In order to make a good contact with the carbon and the holder, the carbons are "silver tipped"—that is, first copper plated, then dipped into solder, which solders the zinc protruding from the holder end, to the carbon. Such a connection is a permanent one, and is far superior to the scheme of simply bending the zinc over at the end of the carbon, as the zinc becomes brittle when the core is dried and is liable to break off.

We now come to the question of desirable operating characteristics for a flame arc carbon. First of all, such a carbon should be reliable. It has been pointed out by Steinmetz[5] that after high efficiency is attained, we can afford to sacrifice some of the efficiency for reliability, and other desirable factors. As will be shown below, the flame arc is already of high efficiency, hence we place reliability as our first desirable characteristic.

We may consider reliability under the four heads:

1. Constancy of distribution.
2. Constancy of light flux.
3. Constancy of color.
4. Ability to start with cold points after the carbons have been in use.

The length of the arc has a great deal to do with the amount and distribution of light. As the arc lengthens, the voltage increases; it is stated by Hechler[6] that there is a maximum definite voltage for maximum efficiency; that is, some definite arc length gives the most light.

The part that chemistry has had in increasing the reliability may be briefly indicated. It is readily seen that a flame arc which burns brightly part of the time and dimly part of the time can hardy be said to have 100 per cent reliability if all the other factors are high. It may happen that all the flame material is evaporated from a given spot on the surface of the carbon, thereby causing a pure carbon arc for a short time. Such changes, however, are now rare, as a great deal of constructive chemical work has practically obviated this feature.

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[4] Mott, Electrical World, Dec. 13, 1913, p. 1220.
[5] Gen. Electric Review, 17, 180 (1914).
[6] Abstract in "Electrician" (London), 69, 658 (1912).

Another factor affecting the reliability of operation of flame arc lamps is the formation of slag on the points or on the lamp mechanism, and it is readily seen that the proper proportion of the flame constituents and the right kind of addition agents for preventing such slags are of great importance. Here again we find that extended chemical research has resulted in the development of carbons in which this source of trouble has been largely overcome.

It has been mentioned that the flame-arc is of high efficiency. The following figures are from some regular routine tests made in the laboratory:

Lamp.	Current.	Kind of Carbon.	M. S. C. P.	Arc Watts.	Watts per Candle.
Excello	A. C.	Cored—yellow	1,220	363	.29—
Excello	A. C.	Cored—white	843	369	.43—
Excello	D. C.	Cored—yellow	1,462	445	.30
Excello	D. C.	Cored—white	875	450	.51
G. E., Type W	A. C.	Solid —yellow	700	397	.56
G. E., Type W	A. C.	Solid —white	808	394	.49
G. E., Lynn	D. C.	Solid —yellow	1,181	409	.35—
G. E., Lynn	D. C.	Solid —white	939	421	.45

The slightly lower efficiencies with the solid carbons are due to the fact that they are used in enclosed lamps, to which the air has only limited access and so in these lamps there is less oxidation of the carbon and the flame material.

Some work by Henry P. Gage[7] at Cornell University on the efficiency of the arc stream proper may be cited here. This investigator found that, with cored yellow-flame carbons the energy radiated as light from the arc stream was 39 per cent of the total energy radiated by it; with the arc stream from covered white flame carbons, 27.5 per cent of the energy radiated by the arc stream was light energy. The entire yellow arc showed 6 candles per watt radiated, while the entire white arc showed 3 candles per watt actually radiated.

These values are for the spectral region between 3,800 and 6,800 Angström units, and for alternating current, at 13.5 amperes.

The following data may be presented as to the life of flame carbons:

	Life in Hours	
	A. C.	D. C.
Cored—yellow	12.0	12.50
Cored—white	11.08	11.25
Solid —yellow	115.08	125.0
Solid —white	120.0	96.42

These figures show why the enclosed flame arc lamp is more popular than the old "inclined trim" lamp, using cored carbons.

Having indicated at a number of points the important part chemistry has played in the development of the modern flame carbon, let us now take up in greater detail some of the chemical aspects of our topic.

In the first place, the selection of the proper materials for the manufacture of flame carbons is to a very large degree dependent on the chemical properties of these materials. When we consider the carbon base, we find that the chemical behavior, as well as the physical behavior of the various so-called forms of carbon differs with the type of carbon employed. To use an extreme case as an illustration, we know that the chemical properties of graphite differ greatly from those of lampblack. There are likewise similar differences between charcoal and lampblack; petroleum coke and retort coke. This in part accounts for a different carbon base being used for solid and for cored carbons.

To a greater degree than the proper selection of the right carbon base, the selection of the right sort of flame material and the right sort of addition agents with this flame material has been a chemical problem. This is illustrated by the fact that today we know no better material than calcium fluoride for the main constituent of yellow flame carbons. I do not think I will exaggerate the matter in the least when I say that compounds of every compound-forming element have been proposed as proper substances to incorporate into flame carbons—some of them in all sorts of possible and impossible combinations.

Having selected the right materials, the right amount of each is our next chemical problem. That the candle power depends upon the amount of flame material is well known; more exact information on this subject, however, may be had from the following table which is from some work done in our Research Laboratory by Mr. Wm. R. Mott, using cored carbons in an Excello direct-current lamp:

Parts of calcium fluoride by weight...	3	2	1	0
Parts of other salt by weight.......	0	1	2	3
Mean spherical candle power........	927	1,058	765	574

As is seen, there is a maximum per cent of each of the constituents which will give the most light. This is true with nearly every substance which may be added to the calcium fluoride, and when we consider that flamers contain three or more substances in addition to the main constituent, it is readily seen that the nice adjustment of all these substances to each other presents some very interesting problems. It also explains why so much of our knowledge has been obtained in an empirical way. It is, of course, understood that the maxima for different addition agents do not coincide.

The chemical control of the impurities present in the raw materials is of great importance. Silica, ferric oxide and alumina, as is well known, are common impurities in calcium fluoride, and it so happens that too much of these impurities will make a poor burning carbon. Silica is especially undesirable as calcium silicate is very non-volatile and so is a frequent cause of slag formation. The analytical difficulties in determinations of fluorine, silica and rare earths in presence of each other and of carbon are very great.

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[7] Phys. Rev., 33, 111 (1911).

The unbaked carbon is a poor conductor of electricity. It is also rather friable. In the baking, the binder is coked and the carbon is rendered homogeneous and conducting. This coking of the binder is the chief chemical change occurring in the manufacture of the carbon.

We now have to consider what chemical changes may occur during the burning of a flame carbon, and how these may affect the light emitted from the flaming arc. There are three possible sources of light in the flaming arc: electro-luminescence, thermo-luminescence, and chemi-luminescence. We do not know to what extent these three factors affect the light radiation in any one case. We do know, however, that in general, there are two types of flaming arcs, (1) those in which the outer sheath seems to be intensely luminous, (2) those in which the core of the arc seems to be more luminous than the sheath. With very few exceptions arcs of the latter type give light of the shorter wave lengths. An arc into which calcium fluoride is introduced is a representative of the first type; an arc into which chromic oxide is introduced is of the latter type.

King has recently reported[8] that in a tube furnace almost all of the spectral lines seen in the arc spectrum of titanium appear, so that it would appear that in some cases a large proportion of the light from an arc is due to thermo-luminescence, though all possibility of chemical change was not precluded by these experiments.

Oldenberg[9] has made a spectro-heliographic study of various arcs, with some interesting results: For instance, he concludes that in the sodium arc, lines belonging to the principal series such as the "D lines" are due to chemical reactions between the vapor and the air. Band spectra seem to be of two types: those of the first type are due to collisions of atoms in the high temperature core of the arc. The cyanogen bands always seen in a carbon arc he ascribes to collisions between carbon and nitrogen atoms. Bands of the second type are found in the sheath of the arc; they are due to undecomposed molecules; the bands of the calcium fluoride spectrum are of this type. When we consider that the flaming arc is a miniature electric furnace; that Fremy[10] showed years ago that oxygen converts calcium fluoride into calcium oxide; that calcium oxide and carbon react to give calcium carbide and carbon monoxide, and that the other constituents of a flame carbon may react with calcium fluoride, with the carbon, with each other and the atmospheric gases, we see that it is possible for chemical changes to play an important part in the production of the light of the calcium fluoride arc. Each of the possible substances may play its part in this light emission.

In conclusion, I think we may safely say that the past progress made in the flaming arc art has been due to the co-operation of the chemist, the physicist, and the electrical engineer; the future progress will likewise be dependent upon their combined efforts.

It might not be out of place to point out that the behavior of any one substance in the arc is determined by the conditions surrounding that substance—it behaves according to definite chemical and physical laws; and that our knowledge of these laws for high temperatures is exceedingly meager. On the other hand, once these laws are learned, it will probably be easier to build lamps to suit the carbons rather than to make a carbon to fit any and every lamp. In the extension of our knowledge of these laws, chemistry and especially physical chemistry will play an important part. If I have succeeded in showing you that without the aid of chemistry the development of the flame carbon would have been well nigh impossible, I shall feel that my labors have not been in vain.

TENNESSEE PHOSPHATE PRACTICE.*

By JAMES A. BARR†

GEOLOGY AND MINERALOGY.

Tennessee phosphates are commercially divided into three varieties: Brown, blue and white. The first two only are now of commercial importance. The white phosphates of Perry county are not being mined at present owing to their pockety occurrence. The white phosphate is the highest grade of the three varieties, running often more than 90 percent tricalcium phosphate.

The brown rock is found in three varieties, grading from the dense almost vitreous gray rock, 76 to 82 percent tricalcium phosphate, down through the ordinary cellular brownish gray rock, looking somewhat like a sandstone, 72 to 76 percent, to the lowest grade of soft mucky blackish brown rock, 72 percent and lower. The solid rock occurs in layers much broken up by joints filled with a corresponding grade of phosphatic sand, clay being the chief impurity.

The blue phosphate looks like a granular bluish limestone. It also varies as to color, the grayish variety being highest in grade, averaging 72 per cent; the darker blue runs 72 percent and lower.

The brown phosphates of the Mt. Pleasant district occur in Bigby limestone of the Ordovician period. In Giles and Hickman counties the brown varieties occur in the Leipers limestone of the same period. Both limestones are a bluish crystalline variety often showing a banded structure upon weathering. These limestones are phosphate bearing often to the extent of 35 to 40 percent, and are occasionally used as a low-grade fertilizer or for a filler for the manufactured fertilizer.

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[8] Astro-physical Journal, 39, 139 (1914).

[9] Zeitschrift für Wiss. Photog., Photophysik und Photochem., 13, 133 (1913).

[10] Ann. Chim. Phys. (3), 47, 17 (1856).

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†Mt. Pleasant, Tenn.

The principal deposits of blue rock, which are of commercial importance, occur between the Chattanooga shale and the Ordovician limestone, also phosphatic and of the same character as those just described.

PROSPECTIVE AND VALUATION.

Brown Rock.—The extent, depth and quality of the phosphate deposits are commonly determined by boring with earth augers and post-hole diggers 4 in. in diameter. Test pits are also employed in conjunction to give a better idea of the character of the strata.

In blanket deposits the holes are sunk 200 ft. apart in squares while in hat-brim formations (ring deposits on a hill side), the holes are spaced 200 ft. on the long axis of the deposit and 50 to 200 ft. on the short axis, the latter spacing depending upon the width between upper and lower boundaries.

Since the overburden is not excessive, rarely being over 30 ft., the light and cheap 4-in. earth auger gives good results with two operators; ¾-in. pipe in convenient joints is used for rods. The post-hole digger is used for penetrating hard substances like flint or plate phosphate rock. It is merely a form of hollow drill, with a 4 by 12 in. barrel of ⅛-in. steel. When penetrating phosphate a sample or disintegrated core is brought up by the tools and must be removed each time when full, necessitating frequent removals of the diggers from the hole.

About every 400 ft. a pit is sunk to obtain a sample of rock for recovery tests. This will be representative of the rock as mined by hand and sent to the washers, and will also give the true ratio of sand to lump rock with their respective analyses, which is of considerable importance.

The samples from prospecting are prepared for analysis by hand washing in an ordinary wash tub, saving the sand by decantation and separating the lump with the aid of a hose and a ⅛-in. slotted screen. The recovered products are dried, weighed and analyzed separately. The percentage of recovery is calculated from weights in the usual manner. The weight of a cubic foot of phosphate in the ground should be determined so that the percentage of recovery as found may be converted into such convenient terms as 1 acre 1 ft. deep (43,560 cu. ft.).

Cost.—The cost of prospecting will average 7 to 7½ cts. per foot of hole with augurs or $1.50 to $2 per acre for average conditions.

Tonnages are usually calculated on the basis of a recovery of 1,000 tons dry rock per acre-foot for high-grade deposits, but for the average grades this will be more nearly 850 tons per acre-foot. For more accurate work the percentages of recovery should be used as determined in the laboratory, allowing 15 to 20 per cent in actual mining and treatment.

Especial care is necessary in determining the average thickness of rock for unit areas when the deposits are known to lie in cutters. The phosphate will constitute from 30 to 50 per cent of the total volume below the surface of the lime table.

The percentage of iron and aluminum oxides remaining in the washed product has an important bearing on the valuation of the rock. The usual guarantees are given below. For each per cent in excess of guarantee, 2 per cent of *BPL* is deducted.[2]

BPL Per Cent.	$Fe_2O_3 + AL_2O$ Per Cent.
70	6.5
72	5.5
75	5.0
76	4.5
78 to 80	4.0

The total final cost of dry rock f. o. b. cars may be estimated as $2.50, but with a good deposit and modern plant a cost of $2 should be obtained. The resulting profit as determined from the valuation of the rock less working costs should not be less than 20 per cent per annum on the total investment which will be: Property; this cost will average 25 cts. per ton of rock in the ground, or if on a royalty basis, 50 cts. Plant; capacity 75,000 tons per year, $150,000. Mining equipment, $30,000.

Blue Rock.—Since blue rock in the known commercial deposits lies mostly under a stratum of shale, the prospecting is necessarily done by diamond drills or drills of the Calyx type. Both give satisfactory results. The outcrops are usually exposed by shallow test pits. Since these deposits are continuous in one direction, to any great extent, the long and short axes of the deposits are determined at the outset, by tracing the outcrops in gullies. This information materially aids in keeping down the cost of prospecting.

The minimum thickness of the vein for profitable mining at present prices is 24 in.

The sales price of blue rock f. o. b. cars Mt. Pleasant, Tenn., is: 68 to 72 per cent *BPL* with 2 to 2½ per cent iron and alumina, $3.50 to $3.75. The lower grades of 62 to 68 per cent *BPL* are usually sold ground 80 to 90 per cent through 100 mesh at $3.50 to $4, of which 50 cts. represents the charge for grinding.

The cost of equipment and dead development work will be practically the same as given under cost of plants for brown rock, for a plant having a capacity of 300 tons in 12 hours.

The cost of blue rock f. o. b. cars with a modern plant averages $1.80 to $2 per ton, to which must be added with some deposits now being worked 25 cts. a ton to bring the price as quoted f. o. b. cars at Mt. Pleasant, because of extra freight rates.

BROWN ROCK MINING AND TREATMENT.

Removal of Overburden.—Occasionally narrow benches are stripped by hand methods. The dirt is more or less undermined by the removal of the underlying rock, and the bank caved over into the previously mined out bench by prying with a long rod from above.

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[1] A ton of dry phosphate is 2,240 lb.

[2] BPL is the local term for bone phosphate of lime or tri-calcium phosphate, $Ca_3P_2O_8$.

Scattered deposits are stripped by scraper outfits such as are used in railroad work. The outfit usually consists of 5-wheeled scrapers with a hook team extra and a plough team. The work is contracted at 14½ cts. per cubic yard.

The major portion of the stripping is now done by Class 14 Bucyrus drag-line excavators mounting a 70-ft. boom with a 1½-yd. bucket. This machine is adapted to the removal of overburden that does not average more than 15 ft. With more than this depth the pits become too narrow at the bottom.

In Hickman county where the overburden averages 30 ft. a Class 24 drag-line machine is being installed. This has a 100-ft. boom and a 3½-yd. bucket.

The cost of operating the Class 14 machines is:

	Per Shift.
1 Runner, $150 per month	$ 6.00
1 Fireman	2.50
1 Teamster	1.75
1 Ground man	1.50
1 Foreman	3.00
1 Team (owned by company)	3.00
Coal, 2 tons @ $2.40	4.80
Cable wear	5.00
Repairs, oil, and supplies	3.00
6 per cent interest on $13,000; 250 shifts	3.20
10 per cent depreciation	5.20
Total	$38.95

The above is for a machine having caterpillar traction for moving. If a timber and roller machine is used an extra ground man is required.

The capacity averages 1,000 cu. yds. per 10-hr. shift, although often 1,300 to 1,400 yds. are dug under favorable conditions.

While the larger-size machines average more in yardage the operating costs also increase so that the cost per yard is nearly the same.

Two mines use hydraulic stripping because the depth of the overburden is excessive in one and the mining conditions require it in the other. The cost averages 7 cts. per cubic yard.

The bank is cut down by a hydraulic monitor using a 2 or 2½-in. tip. The water pressure usually needed is 150 to 175 lbs. per square inch. The water flows back from the face carrying from 10 to 20 per cent solids, into a pump well. From the sump the water and overburden are pumped to the waste ponds by an 8-in. direct-connected motor-driven centrifugal pump. The pump requires from 1,500 to 2,000 gals. of water per minute for full capacity, with a motor power of 75 h. p.

Mining.—In the Mt. Pleasant field, the rock is mined by hand since the rock occurs partly below the top of the lime stratum, in cutters of irregular shape. Steam-shovel mining has been tried but is not favored because it does not permit hand sorting of clay and flint in the mines.

The rock, being soft and well jointed, is broken with an ordinary hand pick, and shoveled into 3-yd., 36-in. gauge tram cars. The miners use mostly a 10-tined fork where the cast is short but prefer a long handled shovel when throwing up from the bottom of cutters.

The work is done chiefly by contract, the price being 25 cts. per tram when one handling only is required. Where two casts are required, 35 to 40 cts. per tram is paid. The miners keep the track up to the mining face.

In Giles county some deposits are 20 to 30 ft. in depth without interfering lime boulders or cutters. These have been mined by steam shovel but results were not satisfactory because of impossibility of sorting out clay and flint at the mines, which resulted in low grade of rock at the washer. The grade of deposits, now being worked on the lower outcrop, should improve further back in the hill as is the case with most Tennessee rock. Hydraulic-mining methods seem more suitable than steam-shovel operations, in this case.

In Hickman county, because of the depth of the cutters, from 20 to 40 ft., hydraulic mining is successfully employed.

The same equipment is employed as described under hydraulic stripping.

The centrifugal pumps used are of very rugged construction, being the same as employed in the Florida pebble district. The shell is of heavy cast iron, and when worn out it is rejected this being found more practical than the use of liners. The other wearing parts are the end plates which are easily replaced. The shaft is protected from grit, which gets into the stuffing box, by a stream of pressure water. The stuffing box is submerged in a water seal to prevent air leakage. A bearing of ample proportions, with ring oilers and oil reservoir, takes the weight of the shaft and overhanging impeller. The motor is connected to the pump shaft through a flexible coupling, the entire unit being mounted on one base plate. The motor is usually a three-phase, 60-cycle, 2,200-volt, wound-rotor type, operating at 500 rev. per minute with drum controller and grid resistances for continuous duty from half to full speed.

The pump is connected to the suction and discharge lines through heavy rubber tubing called flexibles. Steel tubing with peaned flanges is commonly used for all lines.

Transportation.—In the case of hand mining the loaded trams are hauled to the plant by saddle-tank locomotives usually of the 17-ton class for main-line hauls and 12-ton for yard and mine switching. The 17-ton dinkey can haul 30 cars on the average mine-track while the 12-ton can handle 20 cars.

On both main line and mine sidings 40-lb. rails are mainly used, but 30-lb. rails are more often used in the mines.

Washing.—The tram cars are hauled up an incline by a belt-driven hoist to a tipple where the muck is discharged, with the aid of water, if necessary, into a crusher hopper.

The crusher is of the single-roll type, being more of a disintegrator and feeder. Enough water is sprayed in at this point to enable the crusher to pass a tram load through every 2 min.

The crusher discharges into the low end of a log washer, 25 ft. long, set on a slope of 1 in. per foot. The solids are carried forward and up the slope by the paddles of the log which are set on an angle of 45°, at the same time being subjected to a very thorough mixing so as to emulsify the clay, some of which is carried back with the water and phosphate sand to the tail of the log where it overflows an adjustable tail gate, into a launder leading to the sand washer.

Log No. 1 discharges into a second log washer, where fresh water is added.

Log No. 2 discharges into a conical trommel, 30 and 60 in. by 17 ft., having a ½-in. metal jacket with 1½-in. round perforations, which merely acts as a shell for the screen, and support for the inner lining jacket of ⅛-in. metal having ⅛ by ¾-in. slots. A 4-in. pipe extends through the center supplying water under pressure through ¼-in. holes; the water jets are directed against the rock, and effectually remove the undersize and remaining clay.

The undersize of the trommel goes to the sand washer. The oversize is discharged on to a picking belt where the clay, flint and limestone are removed by boys. The picking belt discharges to the wet storage system.

The principal tonnage of phosphate rock is washed according to the above methods. One company uses drag conveyors with perforated bottoms, instead of logs, water being sprayed from above. Another company uses a revolving cylinder with flights serving to mix rock and water, and elutriate the clay.

Sand Washing.—All the undersize from the log or rock-washer department is treated in a separate sand washer. There are three distinct systems used:

1. The sand is washed in a drag classifier of the "El Oro" type locally called the riffle trough. It consists mainly of a double-strand chain flight conveyor with 1¼ by 30 in. flights traveling up a slightly inclined trough, about 40 ft. per minute. The sand pulp is fed near the middle and carried up past sprays of water. This system is not as efficient a washer as could be desired, has high repair costs and a low percentage of recovery.

2. Tank System. (*a*) The sand pulp from the rock washer is run into sand tanks about 10 ft. square and 30 ft. deep. When the tank is full the settled sand is washed out through a slatted opening into the sump of a steam pulsometer pump, which elevates the pulp to the next bin. This operation is repeated five times.

(*b*) Same as (*a*), but the operation is made continuous by hydraulic ejectors or jets, as they are locally called, to pump the sand, as it settles into the succeeding bin. This system avoids the use of expensive pulsometer pumps but requires more water, using 700 gals. per minute to pump 80 to 100 tons of sand in 11 hrs.

3. The pulp is fed into the high end of an inclined revolving cylinder provided with internal flights for agitation of the charge. A counter current of wash water is supplied to carry off the elutriated clay. The sand is discharged at the lower end by a spiral and further dewatered in an intermittently discharged settling box. The overflow from the settling box and cylinder washer is further settled in a tank with transverse baffles. The sand caught in this tank is washed out through holes in the side to a drainage pond.

A new plant is now being designed that will use a dewatering tank the underflow of which will be jetted into a series of Dorr classifiers, fresh water being added to the dewatered sand before feeding into the succeeding classifier, the final dewatered product going to the wet storage system. Two of the rakes near the head end of each classifier will be replaced by spray pipes. This system has been tested out with excellent results and low water consumption. The overflow from all the above will be settled in a large 20 by 60 ft. tank. The product settled in these latter tanks will be washed separately either in Dorr classifiers or in Dorr thickeners with sprays on the arms.

Wet Storage and Drainage.—Since the material comes from the washers with 25 to 30 per cent moisture, it is very important to provide a drainage system. By storing from two to three weeks the moisture content is reduced to 20 per cent, saving from 2 to 2½ cts. per ton of rock in coal alone for drying, besides increasing the capacity of a 60 in. by 40 ft. dryer from 90 to 150 tons in 11 hrs.

In the older style plants the storage is done in tanks or by building up in dumps with tram cars. The former is necessarily limited in capacity and the latter rendered expensive on account of the amount of labor used. In the modern plants, electric cranes operating clam-shell buckets are used.

One 10-ton electric traveling crane, 60-ft. span (with 2½-yd. clam-shell bucket)	$10,000
Steel runway, 40 ft. to top rail, 400 ft. long	10,000
Generator capacity in power house, 40 kw. @ $55	2,200
Total	$22,200
One 30-ton, 8-wheeled locomotive crane, standard gauge, 40-ft. boom, 2½-yd. clam-shell bucket	$14,000
Wooden trestle, 12 by 400 ft.; material used 75 per cent heart L. L. Y. pine, with concrete foundations	4,000
Generator capacity 40 kw. @ $55	2,200
Total	$20,200
One 30-ton steam crane same as above	$10,000
Trestle	4,000
Total	$14,000

With current at 1½ cts. per kw.-hr. and coal at $2 to $2.50 per ton the steam crane can be operated as cheaply as the electric, where alternating current is used, but with direct current the cost is more in favor of the electric unit.

Drying System.—The next step after the storage of the material in the drainage piles is the reclamation of the drained phosphate and the drying of it in rotary driers or kilns.

The driers first used were light in construction, giving trouble from break downs and rapid wear. They were from 52 to 56 in. in diameter and 32 ft. long. The drive was by friction only through the trunnions. Power consumed was high, averaging 30 h. p. per unit including fan. The material was fed into the hot end of the shell. The coal consumption averaged 90 to 100 lbs. per ton of rock dried to 2 per cent moisture with a capacity of 80 tons per drier.

Modern driers, which are fed at the cold end, are characterized by heavy construction such as is used in rotary cement kilns. The size of the unit is usually 60 in. by 40 ft., and the power for driving 15 to 20 h. p., including fan for forced draft. A view of a modern rotary drier is shown in Fig. 7.

These driers reduce 135 to 165 tons of phosphate from 20 per cent moisture down to 2 per cent, for the lower capacity given, and down to 3 per cent for the higher capacity. The coal consumption averages 75 lbs. West Kentucky coal per ton of rock dried.

The dried phosphate is elevated to a sizing screen and storage hopper, by an elevator which is usually a single strand of No. 111 combination chain with buckets every fourth link. A traction head pulley and plain sprockets and idlers are used since the use of sprockets with teeth would cut down the life of the chain 75 per cent. Such an elevator lasts three years in ordinary service.

The phosphate is either chuted directly from the storage bin to railroad cars or else carried out to storage sheds by an electric-driven larry. The older plants use cable-driven cars or push cars.

By storing the rock, advantage can be taken of the residual heat to remove at least 1 per cent of moisture. Cars are sampled at the works so that no credit is allowed for drying out in transit.

The rock is stored in a ground-level shed and loaded into cars by contract labor. This arrangement appears to be crude, but special conditions seem to warrant it.

Overhead reinforced concrete storage 10,000 tons capacity	$80,000
	Per Ton.
Cost of loading from above bin with car loaders	1.8c.
Interest 6 per cent and amortization 6.7 per cent	10.2
Total	12.0c.

The above is based on a 15-year mine life with a capacity of 100,000 tons per annum.

Electric traveling crane	$10,000
Steel shed 10,000 tons capacity with crane way	25,000
Total	$35,000
	Per Ton.
Cost of loading with crane and car loaders	3.9c.
Interest and amortization	4.4
Total	8.3c.

1 Steel shed, 10,000-ton capacity		$12,000
Or wood construction	Per Ton	$5,500
Cost hand loading, contract price	7.5c.	
Interest and amortization on $12,000	1.5	
Total	9.0c.	

The hand loading has the important advantage of being flexible and selective. The loader does not load wet streaks of rock; he throws out any foreign substance, spots and sweeps out his own car. He loads the car to the required capacity or is fined.

The automatic scraper and belt conveyor type of loading equipment would not be permissible on account of not being selective.

Production Costs.—The following were taken from the average costs of a mine during six months of good mining weather:

	Per Ton, Cents.
Mining	0.64
Transportation and team expense	0.23
Washing	0.46
Drying	0.47
Shipping and track expense	0.09
Total, per dry ton 2,240 lbs.	$1.89

MINING AND TREATMENT OF BLUE ROCK.

The outcrop is usually stripped and mined by hand, back to where the overburden does not exceed over 12 ft. on an average. For extensive outcrop mining a steam shovel is used for stripping.

The underground work is done on the room-and-pillar system, the pillars being recovered on the final round by drawing back. Main and cross entries are driven according to the topography, the rooms being led off from the cross entries alternately every 50 ft. The ordinary dimensions of the room are 25 by 200 ft. The long axis of the room is parallel with the rock jointing so as to obtain the maximum effect of the powder in blasting.

Advantage is taken of an overlying layer of low-grade kidney formation between the blue rock and the shale to make an overcut with air drills and to blast to this face. The skull is thrown back into the gob, acting as a support to the roof. Short timbers are used at the face to protect the workers from the shale roof which tends to slab off.

The rock is loaded and mined by the contract system, into cars holding about 3,000 lbs. The loaded trams are pushed to the room entry by hand where they are hauled to the mouth of the tunnel by mules. Here they are made up into trains and hauled to the plant by a 17-ton, 36-in. gauge locomotive.

The surface plant is principally a crusher and drier. The blue rock is not subjected to any washing process.

The order of machinery, etc., in the plant is: Gyratory crusher; 60 in. by 60 ft. rotary drier fed at cold end; crushing rolls set to ½ in.; sizing screen; cable-driven storage larry.

The cost per ton for a modern plant producing 300 tons per 10 hrs. is:

	Per Ton.
Rock at tipple	$1.30
Drying	0.10
Crushing, screening and stocking	0.40
Total	$1.80

FINE DRY GRINDING, BOTH BLUE AND BROWN ROCK.

A considerable tonnage is now being ground for use as a fertilizer direct, or for shipment to fertilizer factories for acidulation.

For phosphate containing lumps ½ in. or more in size primary coarse crushers are used. Following the coarse crushers a fine-grinding mill of the ring roll or Fuller-Lehigh type is used. One company uses a Hardinge mill. The discharge from the fine-grinding mill is elevated to sizing screens where the final size is taken out and the undersize returned to the mill.

Two companies now use tube mills after the fine-grinding mill as described above, to reduce the phosphate to the final size.

The raw rock, for direct application as a fertilizer, is ground to 90 or 100 per cent, through a 100 mesh; for acidulation through a 60-mesh screen.

MANUFACTURE OF ACID PHOSPHATE.

Chemistry.—The final step in the treatment of phosphate rock for the fertilizer trade is its conversion from the insoluble tricalcium phosphate to the more soluble forms, by direct treatment with sulphur acid.

The following are the basic reactions of the process:

(1) $Ca_3P_2O_8 + 2H_2SO_4 + 6H_2O = (CaH_4P_2O_8 + 2H_2O) + 2(CaSO_4.2H_2O)$.

(2) $Ca_3P_2O_8 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4.2H_2O)$.

(3) $Ca_3P_2O_8 + H_2SO_4 + 6H_2O = (Ca_2H_2P_2O_8 + 4H_2O) + CaSO_4.2H_2O)$.

Reactions (1) and (2) are the ones desired in the manufacturing process. With too little sulphuric acid present in the mix reaction (3) takes place, forming more or less di-calcium phosphate, insoluble in water. With an excess of acid, too much phosphoric acid is formed as in (2), resulting in a moist and lumpy finished product.

In determining the amount of acid required, account must be taken of the consumption of the principal impurities as noted below.

Carbonate of lime and magnesia are desirable to the extent of 5 per cent because of the heat furnished in the reaction with the acid, the leavening effect of the CO_2 released and the drying effect on the final product in storage.

Fluorite is broken up by the acid, the resulting fluorine combining with the silica and passing off in part as the volatile H_2SiF_5. When troublesome, this must be properly handled and washed in scrubbers.

Iron and aluminum oxides are the chief constituents that must be carefully handled and regulated. They not only consume acid but result in a moist lumpy acid phosphate, if in excess of 4 to 4½ per cent.

When the acid phosphate does not dry out well, its quality and per cent of available P_2O_5 may be materially increased by adding raw, fine-ground phosphate rock before storage preferably, but also directly before mixing. Some advocate the use of ground limestone but this will cause some of the soluble phosphate compounds to revert to the insoluble, often to the extent of 2 to 3 per cent.

The manufacture of double superphosphates is done by filter pressing out the soluble portions of acid phosphate, and evaporating the filtrate in pans to 45 per cent P_2O_5. The concentrated phosphoric acid is used to treat a fresh charge of raw phosphate rock:

$$Ca_3P_2O_8 + 4H_3PO_4 + 6H_2O = 3(CaH_4P_2O_8) + 2H_2O.$$

This is a highly concentrated product used mainly for export trade.

Manufacture.—The lump and sand phosphate is unloaded from the railroad cars by hand and wheeled in a barrow to the storage pile or to the coarse crusher. From the coarse crusher the phosphate is elevated into feed hoppers of the fine-grinding mills. The mills and the process used are the same as described previously under "Fine Grinding." A mill that is much used, with satisfaction, not previously mentioned, is the three-roll Griffin mill.

The ground phosphate is next treated in a mixing pan, in batches of 1 to 2 tons, the ratio of acid to rock being 1,000 lbs. rock to 1,000 to 1,008 lbs. 50° Bé. acid. One type of mixing pan is a round cast-iron pan revolving slowly, with one or two sets of stirring arms or plows, also revolving but at a higher rate.

When completely mixed, the contents of the pan are discharged through bottom doors into a square concrete or brick chamber below, called a den. Here the reactions continue aided by the heat.

After remaining in the den for about 48 hrs., or until the mass becomes cool, the contents are again discharged through bottom doors, by manual labor, into an elevating and conveying system that carries the acid phosphate to large storage piles.

The manufacturing process is carried on the year around, but shipment is made principally during three months in the spring and two months in the fall.

Before shipping to the consumer it is usual to add enough ammoniates and potassium salts to make up a complete fertilizer.

During shipping seasons the acid phosphate is reclaimed from the storage piles by hand labor, wheeled to the mixing and bagging system. This consists mainly of a disintegrator which breaks up the lumps of the acid phosphate; a screen takes the discharge from the disintegrator and returns the oversize, the undersize being sent to the mixing machine, where it is mixed with the proper amounts of ammoniates, potash salts and filler. The mixed product is bagged in a bagging machine, weighed and delivered to cars by hand.

It will be noted that there is a large amount of hand labor included in the scheme of operation that might be eliminated by properly designed machinery, and such is beginning to be included in modern plants.

The costs vary widely and the different freight rates on acid and rock. To the costs of raw material the additional charges for acidulation, mixing, and shipping are from $1 to $1.25 per ton. There is a loss of about 7 per cent in the manufacture of the acid phosphate that must also be taken into account.

THE PLANT.

THE MORGAN PRODUCER GAS MACHINE.*

The Morgan Construction Co., Worcester, Mass., has developed a producer gas machine that because of radical improvements in mechanical design will convert 3,000 lbs. of coal per hour into gas without hand labor, thus constituting an important advance over existing practice. The manufacture of producer gas has been dominated to a large extent by the idea that a gas-making fire must be frequently disturbed—poked or twisted or broken up—in order to make gas in large quantity. Much ingenuity has been expended on the assumption that mechanical means should be employed in accomplishing results in these ways. The Morgan Construction Co. for some years worked in this direction and various mechanical devices resulted, but it was found that the output was not commensurate with their cost and that they represented no fundamental improvement upon earlier methods. All mechanical means employed to prevent clinker or to break it up inevitably created new variations in the density of the fuel mass.

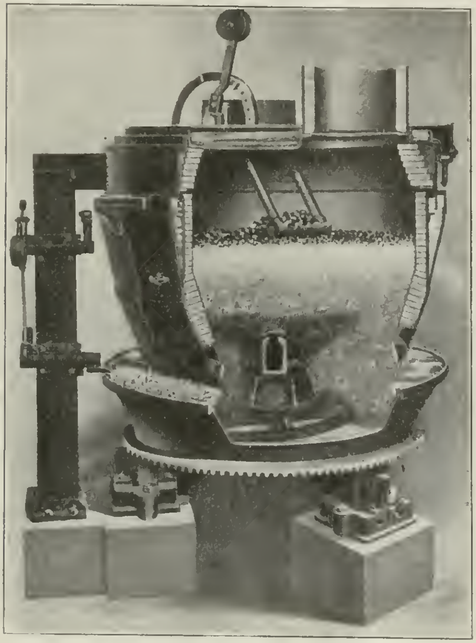

Fig. 1—The Morgan Producer Gas Machine.

The basis on which work was begun on the machine that is now brought out is that if the coal is spread properly and the surface leveled continuously, the fire needs only to be let alone; that later disturbances causing variations in density create hot places, with resultant clinkers and inferior gas. The mechanical leveler, Figs. 1-3, floats on the fuel and permits of any variation in height.

The proper removal of ash is almost as important a factor. In the Morgan machine the ash pan is swept by a spiral-shaped bar or plow, the result being a uniform settling of ash over the whole area. The action is automatic. When the operator desires to remove ash he sets a lever. The plow is held stationary during one complete revolution of the pan and is then released automatically. The ash is discharged at one final point into a conveyor or car. Since there is no agitation and the walls are free from obstructions, the coke is undisturbed and its temperature is maintained until it is consumed, the result being an ash practically free from carbon.

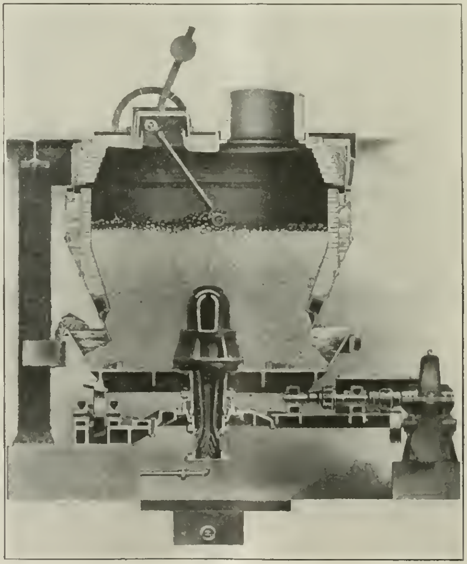

Fig. 2—Cross Section of Producer Gas Machine Showing Leveler in Action.

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*From The Iron Age.

An even distribution of the blast over the gas-making area is essential in order that each square foot of fuel bed shall gasify at the same rate. In designing this machine the central blast hood was discarded as inadequate to the high capacity demanded. Instead, as shown in Fig. 2, the blast is delivered from the three hollow radial arms, around the circumference of the hollow ring, or mantel, the result being a gentle, sustained blast pressure which is evenly distributed over the whole surface.

The company's engineers have found that the matter of firebrick lining has been given relatively little consideration, whereas it is, in reality, an important factor. The inner surface of the bricks should not become sufficiently hot to permit of fusing with the ash and thus create clinging clinkers. The remedy was to reduce the thickness of the firebrick and surround it with a water jacket, which keeps it cool enough on the inner surface to prevent any slagging action.

An important feature of the gas-producing machine is the means of feeding mechanically and with required regularity small quantities of coal. The new feeder, Fig. 4, receives the coal from the bin and charges it in small and uniform quantities at frequent intervals. As a consequence one man can take care of a battery of six machines gasifying 9 tons per hour.

Severe tests of the new features have been made under industrial conditions. With one of the earlier machines of the type, installed by a large steel company, the opportunity was afforded last year to take continuous 12-hour samples of the gas day and night

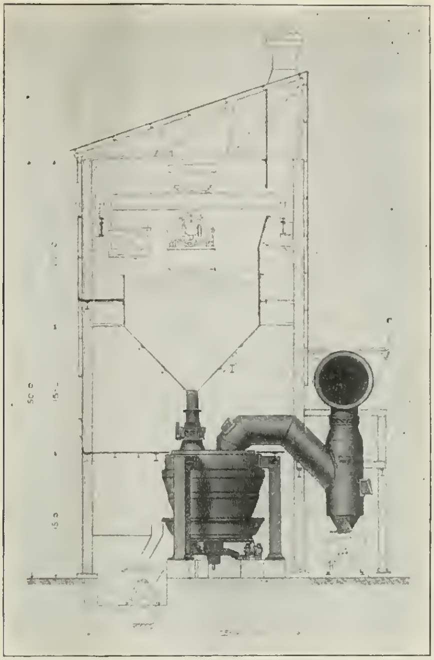

Fig. 5—Cross Section of a Ventilated Gas House With Overhead Coal Bunkers and Crane Service, Showing the Direct Connection With the Feeder.

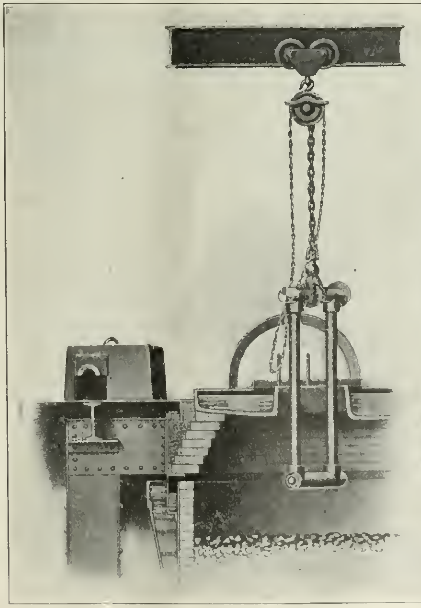

Fig. 3—Removing Fuel Leveler.

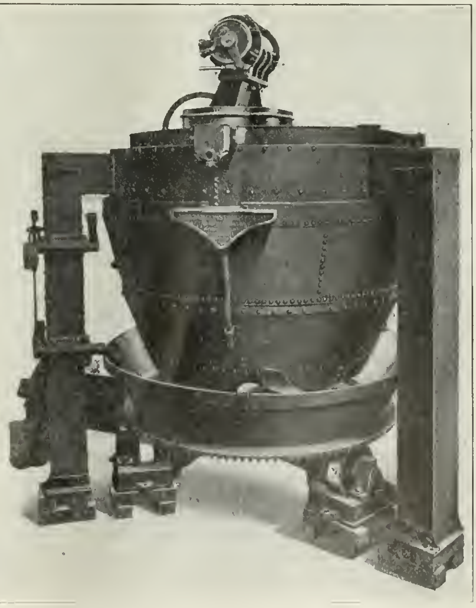

Fig. 4—Extension View Showing Measuring Feeder in Place.

for several weeks. The detailed analyses were made by the works chemist and are noteworthy on account of the low CO_2 and the high heat value and regular quality of the gas. The results for one week are presented in detail in Table 1, together with the averages for the preceding week:

TABLE I.—ANALYSES OF 12-HR. CONTINUOUS GAS SAMPLES.

						B. T. U.	
Feb., 1914.	CO_2.	C_2H_4.	CO.	H_2.	CH_4.	U. S. Steel standard.	Total 32 deg. F.
9 Day	3.0	0.3	25.6	10.5	4.6	158.5	178.5
Night	2.7	0.6	25.8	11.4	2.4	149.0	168.0
10 Day	3.0	0.8	28.0	11.7	3.0	162.5	183.0
Night	3.5	0.4	26.4	11.7	3.3	154.0	173.5
11 Day	2.5	0.8	27.2	11.4	4.0	168.0	189.0
Night	2.8	0.4	27.2	11.4	2.8	151.5	170.5
12 Day	2.4	0.5	28.2	11.4	3.9	166.0	187.0
Night	3.0	0.8	27.5	11.7	1.6	148.0	166.5
13 Day	2.5	0.6	28.5	9.3	4.2	165.5	186.0
Night	3.0	0.8	27.4	11.7	2.9	160.0	180.0
14 Day	2.8	0.7	28.0	10.2	4.1	167.0	188.0
Average	2.8	0.6	27.3	11.1	3.4	159.0	179.0
Average 2-7...	2.8	0.6	27.4	11.4	3.6	162.0	182.5

During some of the periods an accurate account of the quantity of coal gasified was kept. The average was 2,766 lbs. coal per hour for 120 hours from February 9 to 14 with gas of 178 B.t.u. The data by days are presented in Table 2:

TABLE II.—QUANTITY OF COAL GASIFIED IN CONTINUOUS OPERATION.

	Average lb.	Average B.T.U. per Cu. Ft. of Gas.	
Feb., 1914.	coal per hr.	U. S. Steel standard.	Total 32 deg. F.
9 Day	2,800	158.5	178.5
Night	2,740	149.0	168.0
10 Day	2,740	162.5	183.0
Night	2,690	154.0	173.5
11 Day	2,740	168.0	189.0
Night	2,690	151.5	170.5
12 Day	2,800	166.0	187.0
Night	2,860	148.0	166.5
13 Day	2,800	165.5	186.0
Night	2,800	160.0	180.0
Average ...	2,766	158.5	178.0

In another case, where open-hearth furnaces were operated analyses of an 8-hour continuous sample of the gas were made practically every day. These records cover a period of five months and average 3.5 percent CO_2, 28.8 percent CO and 182 B.t.u. The analyses for the week September 21-26, 1914, are given in Table 3 with averages for the two previous weeks:

TABLE III.—ANALYSES OF 8-HR. CONTINUOUS GAS SAMPLES.

						B. T. U.	
Sept., 1914.	CO_2.	C_2H_4.	CO.	H_2.	CH_4.	U. S. Steel standard.	Total 32 deg. F.
21	3.5	0.9	28.8	12.3	2.6	165.0	185.5
22	3.3	0.9	29.9	12.2	2.6	168.5	189.5
23	3.1	0.9	30.1	12.9	2.4	169.0	190.5
24	3.2	0.8	29.2	11.1	2.6	161.5	181.5
25	2.8	0.9	29.9	12.6	2.6	169.5	191.0
26	4.0	0.8	27.6	12.4	2.7	160.5	180.5
Average	3.3	0.8	29.2	12.2	2.6	166.0	186.0
Average 8-12..	3.5	0.7	29.8	11.6	2.7	165.5	185.0
Average 14-19.	3.6	0.8	28.7	12.1	2.6	163.0	183.0

Recently the same owners desired to determine on what gasifying capacity they could safely count as a guide to their future requirements. After increasing the rate to 3,260 lbs. coal per hour they decided they could safely rely on a working capacity of 3,000 lbs. per hour. The results are given in Table 4:

TABLE IV.—GASIFYING CAPACITY OF 10-FT. PRODUCER GAS MACHINE.

				B. T. U. of Gas.	
Sept., 1914.	Net tons coal per day.	Operating hours per day.	Coal per hr., lb.	U. S. Steel standard.	Total 32 deg. F.
21-22	32.35	23.70	2,730	167.0	188.0
22-23	36.00	23.05	3,120	168.5	190.0
23-24	34.15	22.05	3,100	165.0	186.0
24-25	37.35	22.90	3,260	165.5	186.5

Measurements taken during several weeks showed a consumption of 1/6 lb. of steam per lb. of coal. The power required to operate the machine is ¾ hp. at the driving gear for each machine as a uniform load, with the exception that for 15 minutes each 12 hours, while plowing ash there is an increase to 1½ hp. Operating parts are designed in accordance with the Morgan rolling mill practice, with bearings provided with bushings to facilitate renewals, and protection from dirt and dust and positive lubrication are included in the design.

INCLINED RETORTS.*

By R. B. RICHARDSON.

The development of the Inclined Retort System on a practical scale was begun by Coze in the city of Rheims. His retorts were laid, as now, at an angle of 32°. The charging mouthpieces were curved extensions of the retorts, all brought up to the same level. The chief objection to this design was that the coal passed through the mouthpieces at different velocities, depending on the location of the retort. This made equal and uniform charging nearly impossible. In another early design, the retorts sloped at 45°, which facilitated drawing and allowed a full charge; this was the first successful demonstration of a retort completely filled with coal.

The greatest difficulties in designing inclines have been in securing uniformity in charging and heat distribution. The charging was perfected by doing away with the elongated mouthpieces and charging the coal from individual lorries at an equal elevation. The tendency of the heat to run to the back of the bench was controlled by dividing the combustion chamber into two compartments provided with separate carbonmonoxide nostrils and air ports. Inclined retorts were formerly built of clay, in two or three sections, laid in settings of clay. The failures have been largely due to the inability of the clay to resist the high temperatures of modern operation. The use of clay has been almost entirely discontinued and settings are now built of silica blocks, with retorts of silica tiles. Silica neither shrinks nor fuses at high temperatures; the settings remain firm, the retorts straight and the joints tight, all of which makes for long life and perfection of operation.

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*Paper read before Illinois Gas Association.

The trouble with leaking mouthpieces has been entirely overcome. These are now of improved self-sealing, full sized, D-shaped type; bolted to cast iron heads which enclose the ends of the retorts; rest on the face wall, and are held rigidly in place by wedges driven against steel rails.

The hydraulic main and connections have undergone some improvements, perhaps the most important the individual section gas take-off, and overflow seal for each bench. This prevents troubles due to bad alignment and permits perfect isolation of any bench. The tar and liquor run off together and are separated later, which simplifies the displacement apparatus and alleviates the danger of a sudden general loss of the seal. The gas is generally taken off at the lower or discharging ends of the retorts, but in some instances the standpipes are placed at the charging end, which allows a shorter pipe with a consequent advantage in cleaning.

The generators project from the face of the bench and are located at either front or rear, depending on the fuel used and whether it is charged cold or hot. The latter system is generally preferred, especially since the development of apparatus for handling hot coke. This consists of a movable chute which guides the coke as it falls from the retorts directly into the generator. The generator head and lid are of a pattern designed to pass a large mass of coke, permit easy opening and closing, and resist the action of sudden temperature changes.

Of late the inclined idea has been extended, and two recent installations are distinct departures from the first conception, both successful attempts at carbonization in bulk. The first modification is known as the chamber retort, which is rectangular in cross section and inclined at 40°. These chambers carbonize about 1,600 lbs. of coal in 8 hours, about twice that charged in a D-shaped retort. Since 6 of these may be placed in an arch designed for 6 retorts, they practically double the capacity of a bench, and offer an expeditious plan for increasing the capacity of an old plant. The other proposition is an inclined chamber oven that carbonizes 5,500 lbs. of coal in 12 hours, and produces a good grade of metallurgical coke.

In the Spring of 1913 the old horizontal stop-ened benches in Decatur were approaching the end of their natural life. After carefully investigating modern carbonizing plants and visiting up-to-date installations of various types, it was decided that inclined sectional silica retorts, with silica settings, would operate with minimum labor, bench fuel and repairs and produce maximum quantity of high quality gas per ton of coal. Additional land adjoining the old works was purchased and a new coal gas unit, with auxiliary equipment, constructed.

The installation consisted of 6 full depth benches of sixes, with inclined sectional retorts 15 ft. long, protected by a house of steel with corrugated asbestos roof and sides. One radical brick stack, 42 ins. in diameter by 70 ft. high furnishes draught for all the benches. There is also a steel coat trestle crossing a concrete coal storage pit, coal and coke handling machinery and the necessary gas, steam and water pipes.

The coal is received in hopper-bottom cars, which are dumped into the storage pit or track hopper. This is shown in Fig. 1. From the hopper the coal is carried by a steel apron conveyor to the crusher, from which it falls into a bucket elevator and is carried to the overhead 150-ton storage bunkers in the retort house. From here the coal flows through four valves into three traveling larries, from which it is fed into the retorts.

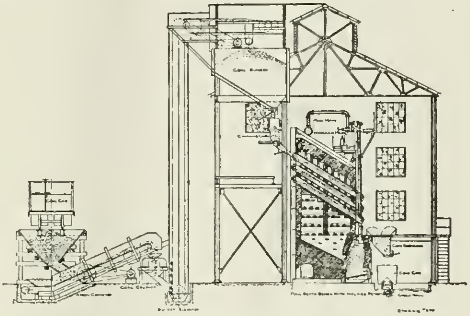

Fig. 1—Cross Section of Installation.

When discharging retorts the coke falls into water-sealed quenching bins, and after it is quenched and cooled is discharged into a coke car, which is raised on an electric elevator, run out on a steel trestle and dumped into freight cars, wagon-loading bins or in the coke storage yard. The coke used in the furnaces is charged direct from the retorts into the generators.

The flushing apparatus for the hydraulic main consists of a steel separating tank that receives the tar and liquor from the hydraulic main, and an ammonia pump that forces the hot weak liquor through jets in the bottom of each of the six separate hydraulic main sections; pitch, carbon and heavy tar are forced out at the tar and liquor overflow.

The contract for the retort house, with all contained benches, apparatus, connections and the coal and coke machinery was awarded the Gas Machinery Co. of Cleveland, O. Four of the six benches were put in operation June 1, 1914. Later the fifth bench was put on and they have been in continuous operation ever since.

The five benches are operated with four men and a foreman on the day shift, and two men and a foreman on the night shift; the same crew could easily operate six benches. The three stokers charge and discharge the retorts, fill the furnaces, clean the standpipes, quench the coke and put it into cars for shipment or in storage bins or yard. One man elevates the coal and cares for the coal elevator, while another cleans all the fires, recovers fuel from the ashes and keeps the grounds in order.

At present we are carbonizing 800 lbs. of coal per retort in six hours. Ten retorts are drawn and charged every two hours, two being opened together. The charging man lights the doors off at the top, while the two men below open the lower doors, scrape the joints, auger the standpipes and pull the stoppers. The coke generally slides out of its own accord, but if it sticks because of a green end or a choked retort, the men below loosen it with light rods and the man above starts it down. When the coke is all out the men below put in the stoppers, close the doors, and the man above opens the larry and runs in the coal. This operation requires but little practice to get in a uniform charge of the proper length. During the drawing, the generators are charged with hot coke from the retorts. The coke that falls into the quenching bins is left there until just before the next draw, drying out. The standpipes are reamed out thoroughly from the top once every 24 hours and augered from the bottom every draw.

We carry a temperature of approximately 2,300° F. in the combustion chamber and 1,900° to 2,000° in the retorts.

The dip pipes are sealed four-tenths of an inch and the foul main is under a vacuum sufficient to maintain a neutral condition in the standpipes. Results covering three months are as follows:

Yield of gas per pound of coal carbonized........	5.5
B. T. U. per cubic foot.........................	595
Average make per man in retort house..........	85,000
Gallons of tar, net ton of coal....................	12.5
Pounds of ammonia per net ton.................	4.26
Pounds of bench fuel per net ton................	355
Pounds of coke per net ton........................	1,300
Daily make per bench on six-hour charges........	101,800

The ammonia yield is not satisfactory, but it is increasing, having run 4.45 pounds during the last month of the period. The low yield at first was due to leaks, and the installation of a new concentrator.

The bench fuel is high, due to high ash content of the coke and extremely hard clinker. On this account, the generator doors are kept open too long for cleaning; and the available grate surface does not remain constant, thereby preventing nice control of the combustion.

The average make per man does not compare favorably with other similar plants, because the men have to move the coke from the retort house to the bins and storage yard.

The following is data for similar installations:

	11 Months, Jacksonville.	4 Years, Mobile.
Yield of gas per lb. of coal carbonized..	5.20	5.28
B. T. U. per cubic foot..................	593	592
Make per man in retort house.........	102,110	114,000
Gallons of tar per net ton of coal......	12.16	13
Pounds of ammonia per net ton........	4.53	4.3
Pounds of bench fuel per net ton......	263	210
Pounds of coke per net ton.............	1,280	1,300
Daily make per bench on 6-hour charges.	102,960	114,000

Taking into consideration the first cost, operating expense, maintenance and results, the writer believes this style of coal gas plant to be, without question, the best that can be installed in plants making up to 2,000,000 cu. ft. of gas daily.

THE TOWER SYSTEMS OF MAKING SULPHITE ACID.*

In continuation of the article on Technology of the Sulphite Pulp Process reproduced in the preceding number from the *Pulp and Paper Magazine*, G. B. Steffanson proceeds to discuss the tower systems of manufacturing "sulphite acid." The high tower system, is, he says, apparently displacing all other sytsems in Europe, and even on this continent it appears to be gaining much ground.

The high towers are more expensive to install than any of the other systems, and the running cost is somewhat higher because the limestone must be hoisted to the top of the tower for charging, but they offer many advantages in other directions. The acid or gas does not come into contact with any pumps or valves before it is ready to be conveyed into the storage tanks, and therefore many costly repairs and renewals are avoided.

The system consists of four or more round tanks, 100 to 120 ft. high or even higher, usually 8 to 10 ft. in diameter, made of hard acid-resisting wood. The tanks are slightly tapering upwards, and are lined with acid-resisting brick or boards, in order to avoid wear and tear of the tanks by the limestone.

The tanks are joined, and surrounded with a wooden structure, to form a tower, divided into a convenient number of floors, from which the tanks can be entered if this should prove necessary. The different floors are connected with the ground and with the top floor by means of stairs and a limestone hoist, as well as a passenger lift.

A water tank is placed on the top of the tower, which should be of sufficient capacity to supply the tower with water for a few hours, in case the water supply should break down. The water in this tank is also used for washing out the tanks periodically in order to free them from materials which might spoil the draught. This tank is, if possible, supplied with spring water, by means of a pump. This pump, and the hoist and lift, are the only pieces of machinery in connection with the tower.

The high tanks act as smokestacks and no forced draught is required unless pyrite burners are used.

The water is distributed over the limestone in the tanks in suitable quantities by means of sprinklers or other arrangements, so that it is evenly distributed and drips down through the limestone and keeps the surface of this moist.

The limestone in the tanks which should vary in size from pieces the size of a cocoanut to a large cabbage, is supported on stout oak beams about 10 ft. from the bottom of the tanks. A number of beams placed close together are provided about one foot above the outlet for the acid, in order to catch the smaller pieces of limestone falling through the upper coarser grates and hold them till dissolved.

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*From Paper.

The water trickles down over the limestone and dissolves the SO_2, which then dissolves the limestone, finally forming the acid bisulphite solution of the composition already mentioned.

The cooled SO_2 is distributed to the different tanks by means of lead pipes fitted with water seals, so that any one of the tanks can be disconnected from the system. The avid overflows a few feet trom the bottom of the tanks into a settling tank, and is finally pumped or run by gravity into the storage tanks.

The bottoms of the tanks are made to slant towards the mudholes, which should discharge into a sewer, and at the mudholes are usually arranged waterpipes with sprays, in order to prevent the odor of SO_2 when the sludge is washed out.

This washing-out must be done at intervals of from one to four weeks, varying with the purity of the limestone and the design of the tanks, in order to prevent too much sludge from going into the settling and storage tanks. When this tower system is used, the escape of SO_2 at the top of the tower should be carefully controlled, especially in summer time and when cold spring water is not used; the water supply to the tanks should be adjustable from the bottom of the tower.

LOW TOWER SYSTEM CHEAPER.

The system of low towers, 35 to 50 ft. high, with four or more round or square tanks, connected as previously described, is cheaper in first cost but presents many disadvantages. Two tanks are worked together in such a way that the gas rises through the first tower and is passed to the bottom of the second tank through earthenware pipes and finally goes up this tower. In order to obtain the necessary draught the tanks must be closed at the tops and a fan or steam ejector provided on top of the second tank. The weak acid from the second tower is pumped to the first tower. The machinery required for the system is costly to maintain in good order. In these towers the limestone usually rests on beams on the level of each floor of the tower, and the charging done from the different floors. This increases the cost of charging and cleaning considerably.

The charging cannot be done every day, but at intervals of one or two weeks, and thus the acid contains too much lime immediately after charging the tanks, and is deficient in lime before charging, unless the mill is so large that several systems of tanks are in use, when this unevenness of the lime in the acid is eliminated. With regard to water supply, gas connections, acid connections, and settling tanks, the low towers are arranged in the same way as the high towers.

Instead of using towers, four or more tanks can be connected in series, as described in connection with the low towers. This system is very expensive in upkeep, and is in use in only a few of the oldest mills in Europe.

THE CHAMBER SYSTEM.

The cheapest limestone system of all as regards first cost is the chamber system. If the waste gases can be taken to a chimney each system only requires two phosphor-bronze pumps. The apparatus consists of two long, square chambers which are built together and connected, and each divided into eight or more compartments, connected alternately at the top and at the bottom. This system is not automatic. In one chamber a certain quantity of water is admitted, and the other chamber contains weak acid. The gas is drawn down through the next one, and then in the same way first through the chamber containing the weak acid so that it passes up through one compartment and through the second chamber, containing the water. Each chamber has a circulating pump, which takes the liquid from the bottom of the chambers through a pipe with branches going into each compartment. The liquid is spread over the whole of the compartment by means of sprinklers and trickles down through the limestone, which rests on grates a few feet above the surface of the liquid.

When the acid in the first chamber is strong enough, it is drawn off and water admitted. The gas is then drawn through the system in the opposite direction, *i. e.*—again first through the weak acid and then through the water. The reversing arrangements should only be watersealed, as the necessary suction is only ¾ in. of water or slightly more. In a few Scandinavian mills, chamber systems with three chambers are used, and some of the mills work them continuously, in which case it is necessary to add a gas saver so as not to lose too much gas.

MILK OF LIME SYSTEMS MOST USUAL HERE.

The milk of lime systems consisting of closed tanks are the most usual on this continent, but they are used in very few mills in Europe. They all work on the principle of drawing the gas through one or more tanks nearly full of liquid, in which the SO_2 is absorbed and the lime dissolved. These tank systems are undoubtedly the cheapest of all acid-making apparatus from the point of view of first cost, and are very easy to handle, but show several disadvantages. The cost of burning the lime has already been mentioned. The vacuum required is considerable, amounting to more than the combined height of the liquid in the tanks, and the air pumps are large, and need considerable maintaining in order to work properly. The tanks and connections must be kept perfectly airtight. The systems are usually difficult to adjust with regard to the quantity of acid made, except within narrow limits and interruptions in the run cause large losses.

There are three essentially different types—namely, Burgess', Stebbins', and Barker's systems. The Burgess apparatus is usually made in the form of one high tank, which is divided into three parts by means of horizontal partitions. The tank is fitted with a stirrer with hollow shaft and arms. The gas passes through the shaft and the perforated hollow arms into the lowest compartment, and then in the same way up to the upper compartments, being intimately mixed with the liquid when the arms of the stirrer pass through it. Stebbins' apparatus consists of two or more tanks usually arranged in steps, and provided with stirrers and two or more partitions in each tank with holes so arranged that the gas, which is drawn in at the bottom must pass from one side of the tank to the other, so as to come into as intimate contact as possible with the liquid in the tanks. Barker's apparatus consists of a high tank provided with three or more horizontal perforated partitions. The gas is drawn in at the bottom and passes up through the liquid and the perforated partitions.

All these systems are provided with overflow pipes for the acid from a higher tank or compartment to a lower one, and the gas pipes are U-shaped to prevent acid from being drawn from a higher tank to a lower one through these pipes. Milk of lime is admitted contInously to the top tank, and in such quantities that the acid flowing from the bottom tank is clear—*i. e.*, all the lime is dissolved. The composition of the acid is regulated by the quantity of lime charged in the milk of lime tank; care should, however, be taken that the milk of lime is not too rich in lime, in which case large quantities of SO_2 will escape through the suction pumps or ejectors if the acid is run clear.

Low towers for milk of lime are in use in only a few mills in Europe. The system consists of three or more towers 25 to 40 ft. high, connected in series, and each provided with a covered feed tank with stirrer and pump. Artificial draught, giving a vacuum of 3 to 4 in. of water is necessary, and is usually created by means of a fan or a steam ejector. The towers are fitted with stones or pieces of wood, so as to provide a large area of contact for the liquid and the gas. The disadvantage of this system is that the tanks become clogged with calcium sulphate, and the cleaning is expensive, and requires much time, as the gypsum sticks to the filling materials.

Several combinations of the above systems are also in use, but it is outside the scope of this article to discuss them.

When using milk of lime systems for manufacturing acid, it is very important to slake the lime properly. Two methods of slaking are in use. The quicklime is dumped into tanks filled with water provided with agitators ,and the liquid is heated to boiling. The milk of lime is then screened before it is passed into the storage tanks. By the other method the lime is slaked in kollergangs or troughs, with the minimum quantity of water, and is then washed into the storage tanks over wire screens and diluted to proper consistence. The second method requires more labor but saves lime and steam. Milk of lime should always be stored in such quantities that it has time to cool down before being admitted into the acid apparatus, as the absorption of SO_2 by the water diminishes very rapidly with increasing temperatures. The storage tanks for milk of lime should always be provided with efficient stirrers.

The acid storage tanks should be so arranged that any leaks can be readily detected. The tanks should also be covered and fitted with gas pipes leading into the acid-making system, or to the gas reclaiming plant if more convenient.

The acid storage tanks may be made of concrete, sheet iron, or wood-lined, with acid-resisting brick, or even common red brick, well pressed and burnt, set in acid-proof mortar, and with or without a lead lining behind the bricks. Tanks made of hard pine are cheap, and can be used for many years without lining; they can later be lined with brick and acid-proof mortar.

If possible a 24-hour or more supply of acid should be stored, and the storage tanks should be so arranged that the raw acid coming from the acid-making plant, can be blown with SO_2 from the relief and blowing off of the digesters, before it is mixed with the finished cooking acid.

In this connection may be mentioned the cooling of the gas from the digesters, before it is blown into the acid. The cooling of the gas has to be carried far enough to prevent the temperature of the acid from rising to more than 120° F., otherwise calcium sulphite may separate. The gas pipes from the coolers should be so arranged in the bottom of the blowing storage tank, as to produce circulation of the acid, in order to prevent overheating of any part of the acid.

On the other hand the acid should be heated by the gases from the digesters to at least 100° F. in order to save steam.

The gas coolers are either made in the form of lead coils in circular tanks, or an elongated system of pipes of the same diameter as the relief pipes from the digesters, laid in a shallow trough.

Water is preferably and almost exclusively used for the purpose of cooling the gases; only a few old Mitscherlich mills still use the original air cooling in long cast-iron pipes.

The raw materials used in the manufacture of acid should all be tested by a skilled chemist, and any leakage of gas should be carefully guarded against. The escape of any SO_2 from the acid-making apparatus should be carefully checked or else great waste may occur.

For an economical running of the plant supervision in other directions is also essential. The burning of the sulphur should be complete combustion, without a large excess of air being admitted. The pyrite burners should always be kept perfectly airtight, except for the proper inlet of air.

The composition of the gas should be ascertained and the cooking acid should be blown to its correct temperature and composition.

The composition of the waste gases leaving the acid system can be periodically followed by means of Orsat's apparatus, or other apparatus constructed for the purpose. The gas coming from the burners should also be analyzed.

It is essential to arrange automatic self-registering instruments in all places where the content of SO_2 in the gas has to be ascertained. An excess of air in the SO_2 gas causes difficulties, because the moisture in the air admitted, as well as that in the sulphur or pyrite, forms steam in the burners, which causes the formation of sulphuric anhydride (SO_3), which in contact with lime (CaO) forms gypsum ($CaSO_4$). The insoluble gypsum causes deposits and clogging, particularly in limestone systems and this causes considerable loss of sulphur and lime. This trouble seems to have made the limestone systems unpopular when first used on this continent. The gas from the burners in plants which are run carelessly, contains frequently only 7 to 8 per cent of SO_2. The content of SO_2 in the gas should not fall below 12 or 14 per cent for pyrite burners, and can under favorable circumstances amount to 16 or even 18 per cent in gas from sulphur burners. The theoretical amount of about 21 per cent cannot be obtained without sublimation of sulphur, and subsequent clogging of the coolers and waste of sulphur.

Sublimation may occur even with a low proportion of SO_2 in the gas, if the temperature in the burner is too high, and no secondary air is admitted behind the burners, so as to promote the combustion of the sublimed sulphur in the combustion chamber.

It is of great importance where milk of lime systems are used, to keep the composition of the acid constant, both when it comes from the acid apparatus, and when it has been blown with gas from the digesters. It has in most of these systems proved impossible to make an acid of proper strength without considerable loss of SO_2, and to remedy this, separators have been used to separate condensed steam from the SO_2 gas coming from the digesters, and in this way get the blown acid up to proper strength.

In limestone systems this is not necessary. The ratio of free and combined SO_2 should here be kept constant, and the acid should be made so strong that after blowing with the cooled gases from the digesters, without previous separation of condensed steam, it should be of proper strength for cooking, or stronger, as it is easy to dilute it.

In order to get a uniform pulp, and not waste chemicals, the digesters should always be charged with the same quantity of free and combined SO_2, and not, as is very often the case, charged with a certain quantity of acid, regardless of its composition.

Green wood needs a somewhat stronger acid than dry wood. Care should be taken, however that enough acid is charged to prevent burning of the chips in the upper part of the digester.

THE ANALYSIS OF THE ACID.

The analysis of the acid is best done by titration with N/10 iodine solution and N/10 caustic soda solution. One cc. of the acid is diluted, starch solution added and titrated with the iodine, until a permanent blue color is obtained. The blue color is then destroyed by means of a few drops of sodium thiosulphate solution. A few drops of phenolphthalein solution are added, and caustic soda run in until a red color is obtained. The number of cc. of iodine solution added indicates the total amount of SO_2 present, and the difference between double the quantity of iodine solution, and the quantity of caustic soda solution used, indicates the amount of combined SO_2.

Multiplying by 0.32 gives the percentage of free and combined SO_2 in the acid. The percentage of lime (CaO) in the acid is to the combined SO_2 as 28 to 32. This test does not give an absolutely correct result, due to the fact that some of the SO_2 evaporates during the test, and to other reasons, but made with care, this test will give a result accurate enough for all practical purposes.

CAPACITY OF ACID PLANT.

It is difficult to give absolute figures for the capacity of the different machines and apparatus in an acid plant, but the accompanying are approximate figures calculated in tons of pulp per day.

The ordinary retort burner is sufficient for two and a half to five tons production.

Rotary burners are built for all productions up to forty tons. The standard Herreshoffs pyrite burner is sufficient for twelve and a half tons.

The capacity of gas coolers has already been mentioned.

Each tank in a high tower system gives acid for twelve to fifteen tons, and low towers in series, about the same.

Chamber systems are built for up to thirty tons.

Milk of lime systems are built for all productions up to 100 tons.

DIGESTERS AND THE COOKING.

There are two different methods of cooking, heating by indirect steam, and cooking with direct steam. In some mills these systems are combined.

Mitscherlich (extra strong, as well as bleachable) and ordinary strong pulp, is cooked with indirect heating, sometimes in connection with direct steam; ordinary bleachable and "quick cooked" pulp is invariably cooked with direct steam.

The digesters are of varying size and construction. In old mills there are still in use digesters with a capacity of two tons or even less, lying stationary, as well as rotary supported on rollers or on bearings. The most commonly used digester is, however, the standing stationary type of five to fifteen tons capacity.

The best type of this digester is one with the diameter about one-third of the total length, the lower end consisting of a cone of about 60°, ending in a blowout pipe, and the upper end consisting of a cone of about 110°, ending in a good sized manhole. This latter design enables the digester to be well filled with chips in a short time, and without too much work.

Digesters are now without exception lined with single or double layers of acid-proof bricks set in acid-proof mortar, with or without a sheet lead jacket behind. Usually the bricks are three and two inches thick, respectively, in some cases bricks as thin as one and a quarter inch are used, in order to save space, but they are just as expensive as thicker bricks, and do not stand wear and tear as well.

Only nonporous bricks should be used, and they should be set half an inch apart, to make it easy to clean the joints of mortar affected by the acid, and replace it. Well pressed and burnt red bricks are nowadays extensively used for digester lining, but tests should be made, before a new brand of these bricks are used, as bricks apparently nonporous may turn out to be porous when used.

Acid-proof mortar is usually composed of one part of Portland cement to one or two parts of crushed and sifted acid-proof brick, often in combination with litharge and asbestos. In order to make the mortar harden quickly, it is made with a 4° Bé. solution of silicate of soda instead of water, and this silicate of soda is during the first cook transformed into an acid-proof compound. Care should be taken that no part of the mortar hardens before it is put in position in the lining, as it is liable to break up when applied, and form weak spots in the lining.

Where the digester shells are not absolutely tight, one should line the digester first with a jacket of thin sheet lead, perfectly tight, because the acid is liable to work its way through the mortar to every leak. The lead lining, however, has it weak points, as it creeps and buckles from the effect of the difference in temperature and separates the lining from the shell, which must be perfectly smooth inside, in order not to wear the lead out too quickly.

The best way to get a good reliable lining is to see that the digester shell is perfectly tight, at a hydraulic pressure one and a half times as high as the working pressure. The shell is next lined with a one inch layer of mortar which is not brittle—*i. e.*, acid-proof mortar mixed with a considerable amount of asbestos, or fat lime, or both. On this is laid one layer of three inches, or two layers of thinner acid-proof brick.

The joints of the last layer of bricks can be filled in to the depth of about half an inch with a mortar made of litharge and specially prepared glycerin. This mortar resists the acid well but is brittle, and should be examined from time to time and renewed if cracked, in order to prevent the acid from attacking the mortar underneath.

The lining should, at the manholes and pipes, end up against disks, or pipes made of hard acid-proof metal, cleaned but rough, but should not end up against lead. Where lead lining is used the main body of the shell is covered with about one quarter of an inch of sheet lead and half an inch lead at all pipe inlets and manholes.

MISCELLANEOUS FITTINGS.

The necessary fittings are two inlet pipes for steam, at or near the bottom of the digester, blow-off valve right at the bottom, or a manhole where the pulp is discharged by gravity, two outlet pipes for gas at the top of the digester, steam pressure gauge, thermometer pocket, and sample cocks. Sometimes digesters are arranged with only one pipe outlet at the top of the digester, combined with an acid-proof pipe with valve connections to acid pipe, blow-off gas pipes, steam gauge, etc.

In indirect cooking five to eight inlet holes for steam are arranged at or near the middle of the digester, and as many at or near the bottom, each hole provided with a valve and check valve respectively, at inlet and outlet. The inlet and outlet holes are connected inside the digester by means of copper pipes, laid spirally round the digester and supported by acid-proof racks.

The blow-off valve should be of ample size, not less than eight inches, connected to an acid-proof bend on the bottom of the digester. Where there is water available of a higher pressure than the blow-off pressure a water connection should be fitted to this bend, so arranged that the water goes in the same direction as the pulp, but it must be taken into consideration that this cold water gets available rosin to adhere to the fibers and this scheme should therefore not be used where there is a large proportion of rosin in the wood.

Steam can also be used to quicken the blowing off and is arranged in the same way as mentioned for water. The blow-off valve should be so constructed that it gives as little resistance as possible to the pulp.

The pipes from the digesters to blow pits can be made either of thin copper or cast-iron. The pitch in the blown off liquor will corrode the cast-iron pipes and prevent the SO_2 gas left in the liquor from affecting the pipe. Pipes from acid storage tanks to digesters should be made of copper or hard lead, pipes from digesters to coolers should be made of extra hard lead (3 per cent antimony) or even better of copper, which, however, is more expensive. The fittings on the digesters should be made of best quality phosphor-bronze, other acid-proof fittings can be made of cheaper materials.

In older mills where scrap metal is available, and where a considerable crew has to be kept for the Sunday repairs—a crew which it is often hard to find work for during the week days—it will pay to make these fittings. All kinds of scrap metal, old brass bearings, valves, etc., are melted in a graphite crucible, and the zinc well "burnt off." To every 6 lbs. of this burnt-off metal add 10 lbs. of phosphorous tin and 30 to 35 lbs. of scrap lead. Cast at as low a temperature as possible and stir well in the crucible before and during the casting, preferably with well dried hardwood branches with the bark left intact, in order to get the oxides of the metals to the surface.

This metal resists the acid well, and can be used in casting pumps, valves, etc., but should not be used for digester fittings.

Gas pipes from the digesters to the coolers and acid storage tanks should be three to four inches in diameter, depending on the size of the digesters. In case screens are arranged inside the digesters to prevent chips and pulp from plugging the gas pipes, these should be made so that no chips can collect on or near them, as these chips will be burned by the steam during the cooking, and form black specks in the pulp which cannot be bleached.

THE DEHYDRATING OIL PLANT OF NEVADA PETROLEUM CO., CALIFORNIA.[*]

By S. J. HARDISON.[†]

In the fall of 1912, the appearance of water in the oil of the Nevada Petroleum Co., Coalinga, Cal., made necessary the installation of a dehydrating plant to reduce the water below the 3 per cent limit prescribed by the agency.

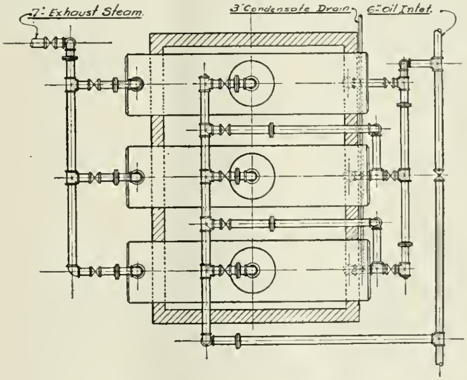

Fig. 1—Plan First Oil-Heating Plant.

Unlike the mining industry, technical literature of the oil industry is limited and extremely unsatisfactory. Until the recent efforts of the Petroleum and Gas Committee of the American Institute of Mining Engineers, no concerted movement has been instituted to secure publication of papers dealing with the problems of the oil business, and because of the additional fact that dehydrating of oil has not been practiced in California to any extent up to comparatively recent time, it was found necessary to experiment in order to determine the most satisfactory plan for this purpose.

It is easy to write regarding successful enterprises, but, while not so pleasant, it is equally desirable to write of failures so that others may be saved the loss incident to such investments.

The water in this oil occurs both free and as an emulsion. Free water easily settles out, but the emulsion requires treatment. So far as can be determined, the emulsion consists of globules of water surrounded and enveloped by a film of oil. Starting with this hypothesis, the theory has been evolved that in order to break up this emulsion the water must be heated at least to boiling point, when an explosion takes place destroying the globule. Unfortunately, this condition was not recognized in the installation of the first plant, which was planned on the following lines:

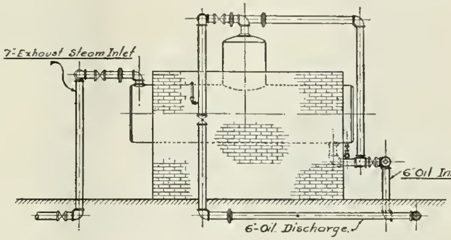

Fig. 2—Side Elevation First Oil-Heating Plant.

A heater was arranged so that all the oil from the wells could be heated before reaching the shipping tanks, these being already fitted with coils for steam heating. Tanks were filled with about 4 ft. of water, live steam was turned into the coils and the water brought nearly to the boiling point, when the heated oil was run in. This for a time was partly successful, but the length of time necessary to apply this heat was too great for practical operating.

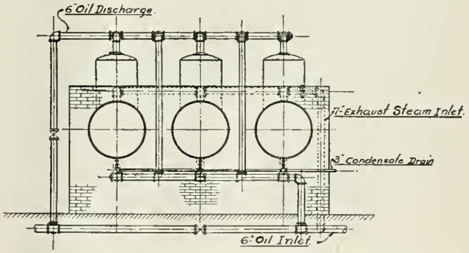

Fig. 3—End Elevation First Oil-Heating Plant.

The arrangement of the heater plant was as shown in Figs. 1, 2, and 3. Three old boilers were suspended on substantial pipe supports, dry brick walls filled up with oil sands being used to prevent radiation on bottom and side of boilers; the tops of the boilers were covered with bats and oil sand after the pipe work was done. Headers of galvanized iron were made to connect the inlet and the outlet steam. Exhaust steam from the compressor and pumps of the central plant was carried through 7⅝-in. casing pipe, connected to the header and thus through the boiler tubes. The outlet was high enough for the condensed steam to gravitate back to the hot-water well of the central plant.

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[*] From Transactions American Institue of Mining Engineers.
[†] Coalinga, Cal.

The plant was placed near the shipping tanks and close to the main line carrying oil from the wells to the shipping tanks.

The piping was arranged so that the oil could be run from the main through one, two, or all three boilers, usually traveling through all three; or the oil could be run direct through all three; or the oil could be run direct through the line as before, in case of leakage in the plant. As no fire was used around this plant, there was no danger from that source.

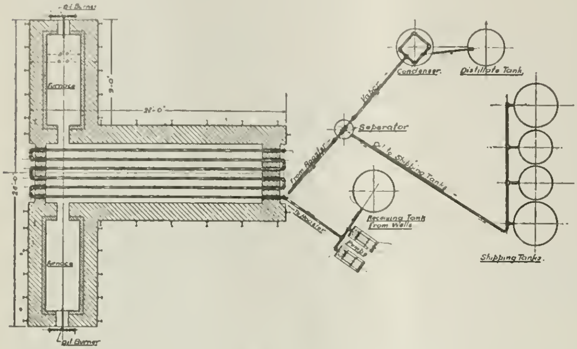

Fig. 4—Plan of Oil-Dehydrating Plant of Nevada Petroleum Co., Coalinga, Cal.

This plant heated the oil to an average temperature of 170° F. very satisfactorily, and with practically no attention or cost, outside of installation. The loss of about 10° in transit to the tanks made about 60° to be supplied by the live-steam coils in the tanks. The water-heating system was not adapted to the conditions and was discarded, the heat then being applied directly to the oil through the coils, but this was also too slow for the necessary operating capacity.

It is certain that the failure of this plant was due to insufficient heating of the oil, and a second plant was built with a view to correcting this difficulty. This plant was constructed as follows:

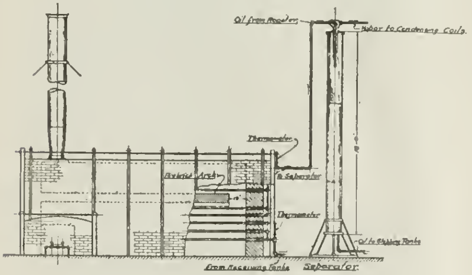

Fig. 5—Side Elevation of Oil-Dehydrating Plant.

Two old 40-h. p. boilers were erected, with the typical oil-field mud setting, the boilers being suspended on pipe supports, with regular oil burners for supplying heat direct under boilers.

The piping was arranged so that oil could be run through either or both boilers, the oil being run in at the bottom and rear, and out at the dome; and again in at the bottom of the second boiler, through it and out to the storage reservoir, from whence it was pumped to the shipping tanks. The heater was still used for this plant, and when both boilers were being used a light fire was carried under the first boiler, the heavier fire being applied to the second boiler. The 6-in. overflow delivery pipe was set on a slight up grade to the receiving tank at the reservoir to insure a back pressure on the boiler.

The gauges usually showed a pressure of a few pounds and a temperature from 230° to 250°, it being necessary to carry it above the boling point.

All piping was 6-in., with no constructed turns or openings in the system. No attempt was made to recover any light products.

While this plant did clean the oil, it was not a commercial success because of the excessive repairs, the sediment from the emulsion settling in the bottom of the first boiler causing blistering within a few days. These blisters had eventually to be cut out and patched and were the cause of several nasty fires owing to the boiler bagging and cracking and the oil running into the fire box.

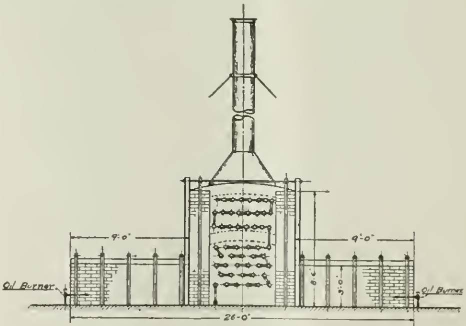

Fig. 6—End Elevation Oil-Dehydrating Plant.

The experiment had now reached such a stage that certain definite conclusions were possible, viz:

1. Exhaust-steam coils cannot be used successfully for heating the oil because the temperature is not raised sufficiently high.

2. If a separation of the oil and water is to take place, the temperature must be raised to a point that will generate steam and cause an explosion in the oil-enveloped globules of water, thereby liberating the water and permitting it to separate from the oil.

The third plant was then built, consisting of brick walls lined with fire brick inside of which were coils of 3-in. pipe through which the oil was pumped. These coils were constructed in horizontal rows of five and six 20-ft. joints below the arch and nine joints in each of the three rows above, 54 joints in all.

Furnaces were built on either side of the front so that the flames would not come in direct contact with the coil. The heat from the furnace passes into the lower compartment, thence to the back and under the arch, then through the opening at the back, into the top compartment and out through the stack at the front end.

A receiver was erected for the oil as it left the roaster, the function of which is to separate the vapor from the oil and to recover the light products that would otherwise pass off into the atmosphere and be wasted. The oil passes out at the bottom of this receiver and into the shipping tanks, the vapor passes out of the top through a coil submerged in cold water, where it is condensed and from which it is allowed to collect in a receiving tank.

This last plant has proved a complete success. Because the coils are small, the solids from the oil cannot precipitate and form blisters. It has been operated daily for the past year without any repairs.

The cost of operating the dehydrating plant per 100 bbl. treated is as follows: Labor, 75c.; fuel consumed, 74c.; steam consumed, 22c.; total, $1.71. The condensation per 100 bbl. is: Water, 10.40; light oil, 0.43; total, 10.83. The gravity of the light oil is 37.2. The oil before treating showed: Temperature, 80° F.; specific gravity, 14.8; B. S. and M., 11.6 per cent. The oil after treatment analyzed: Temperature, 260° F., specific gravity, 15.5; B. S. and M., 1.0 per cent.

JAPANESE SILK EXPORT TRADE LAST YEAR.*

The export trade of habutae and other silk textiles and silk piece goods from Japan in 1914 may be said to have been, generally speaking, prosperous. International events more or less affected this trade, the foreign demand being rather weak for a few months prior to the war, the only exception being January and February. In March and April, the habutae exporters, in addition to the decrease in the demand, were faced with the rise in price of raw silk. The quotation of the Shinshu extra No. 1 raw silk was $482 toward the end of January, while it went up to $493 on February 12, and to $500 a few days later. This quotation was maintained until the end of June. But still the habutae and other silk goods were being quoted far below the margin of profit, and on several occasions the weavers suspended work only to await a turn of the situation. A sign of improvement was discernible in May when the demand was aroused and quotation tended to advance. But this relief was of a very short duration, for no sooner had the exporters realized the benefit of this tendency than came the European war.

As time advanced shipping was reopened, and export to England became possible. So in September the export of habutae and other silk goods to the United States, England, British India, and Australia was conducted rather briskly; and in the last three months of the year the demand was as keen as could be desired, so that the prices rose steadily. Another advantage for the weavers and the traders was that, contrary to this growing demand for the woven silk, the price of raw silk underwent a decided depreciation, so that there remained for them a large margin of profit.

As to the causes of the growth of demand in foreign countries for habutae after the outbreak of the war, it may be pointed out that the American and English firms must have been persuaded to fill the want likely to result from the decrease of productive capacity of the Continental weavers by the importation of Japanese habutae, which, by the way, was very cheap. At the outbreak of the war the foreign firms in Yokohama decided not to accept goods contracted for prior to the war on the ground that the war constituted "force majeure," but the Japanese sellers insisted that the war was no justification for such a decision and urged the firms to carry out their contracts.

This controversy, however, came naturally to an end, because the demand in the foreign market was soon known to be very keen, and the goods were accepted on September and October. Another reason for the growing demand for habutae is considered to be that the war would cause a tremendous number of men to fall on the battlefield, and this would call forth a big demand for silk as mourning dresses by the bereaved families.

No complete statistics for the year's trade in habutae and various silk goods in Japan can yet be obtained But the returns of the Yokohama customs up to the end of November show that there was an export of $14,638,175 worth in plain and figured habutae, kaiki, satin, taffeta, silk handkerchiefs, silk underwear, shawls, etc.

NICKEL-PLATING ALUMINUM.

The successful nickel-plating of aluminum states *The Iron Age* is announced by M. Le Chatelier in a recent communication to the Académie des Sciences. This has not been accomplished heretofore by ordinary methods. The new process consists in a preliminary scouring of the aluminum in a bath of hydrochloric acid containing a certain portion of iron. The iron is precipitated on the surface of the aluminum forming a kind of network. When this is passed into a nickel bath the nickel becomes entangled in this network and adheres strongly to the aluminum. This process is based on a physical action and appears to solve the problem, hitherto considered impossible.

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*Extract from Japan Advertiser of Jan. 7; by Consul General George H. Scidmore, Yokohama.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Written for the Chemical Engineer.

Paint Analysis (Continued).

IRON OXIDES: *Venetian Red, Metallic Brown, Indian Red.*

"Iron oxide is extensively used as a paint. The native oxide naturally varies much in its composition. In general, however, only the poorer grades of native hematite are used as paints. Artificial iron oxide pigments, made by calcining copperas, may be practically pure ferric oxide. Umbers, ochres, and siennas are earthy substances containing iron and manganese oxides and more or less organic matter.

"A satisfactory method for analyses is as follows: Roast 5 grams of the powder, digest with 25 c.c. of hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid, dissolve in water filter, and wash the residue; ignite the residue in a platinum crucible, add sulphuric acid in hydrofluoric acid, drive off the latter, and heat until copious fumes of sulphuric anhydride come off. Add potassium hydrogen sulphate and fuse, dissolve in water, filter from any remaining insoluble (barium sulphate), unite the two solutions, make up to 500 c.c. and use aliquots for the iron and manganese determinations. For the determination of iron place 100 c.c. in a flask, add about 3 grams of zinc, put a funnel into the neck of the flask, heat when the action slackens; if basic salts separate out add a few drops of hydrochloric acid. When all of the iron is reduced, add 30 c.c. of sulphuric acid (1:2), and as soon as all of the zinc is dissolved and the solution is cool, titrate with potassium permanganate.

"For the determination of manganese use 50 c.c., evaporate to a very small bulk, add strong nitric acid and evaporate the hydrochloric acid; add 75 c.c. of strong nitric acid, which should be free from nitrous acid, and 5 grams of potassium chlorate heat to boiling and boil fifteen minutes; then add 50 c.c. of nitric acid and more potassium chlorate. Boil until yellow fumes cease to come off, cool in ice water, filter on asbestos, and wash with colorless, strong nitric acid; suck dry and wash out remaining nitric acid with water, transfer the precipitate and the asbestos to a beaker, add a measured excess of standard solution of ferrous sulphate in dilute sulphuric acid, stir until all of the manganese dioxide is dissolved, and titrate the remaining ferrous sulphate with potassium permanganate. A ferrous solution of about the proper strength is made by dissolving 10 grams of crystallized ferrous sulphate in 900 c.c. of water and 100 c.c. of sulphuric acid (specific gravity 1.84). This solution is titrated with standard potassium permanganate. The reaction taking place when the manganese dioxide acts on the ferrous sulphate is $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + H_2O$. Hence the iron value of permanganate multiplied by 0.491 gives the value in manganese."

RED LEAD AND ORANGE MINERAL.

"These pigments in the pure state are oxides of lead (approximately Pb_3O_4), being probably mixtures of compounds of varying proportions of lead monoxide and lead dioxide. Moisture insoluble impurities, and total lead may be determined by the methods given under chrome yellow; or, in the absence of alkaline earth metals, the lead may be determined as sulphate in nitric acid solution (dissolve by adding a few drops of hydrogen dioxide) by evaporating with an excess of sulphuric acid until fumes of sulphuric anhydride are evolved. Determine as sulphate in the usual way.

"The lead dioxide (PbO_2) may be determined as follows: Weigh 0.5 gram of the very finely ground pigments into a 150 c.c. Erlenmeyer flask. Mix in a small beaker 15 grams of crystallized sodium acetate, 1.2 grams of potassium iodide, 5 c.c. of water, and 5 c.c. of 50 percent acetic acid. Stir until all is liquid, pour into the Erlenmeyer flask containing the lead, and rub with a glass rod until all of the lead is dissolved; add 15 c.c. of water, and titrate with tenth-normal sodium thiosulphate, using starch as indicator. A small amount of lead may escape solution at first, but when the titration is nearly complete this may be dissolved by stirring. The reagents should be mixed in the order given, and the titration should be carried out as soon as the lead is in solution, as otherwise there is danger of loss of iodine. One cubic centimeter of tenth-normal sodium thiosulphate corresponds to 0.011045 gram of lead dioxide, or 0.034235 gram of red lead (Pb_3O_4).

"These colored lead pigments may have their color modified by the addition of organic coloring matters. As a general rule, such adulteration may be detected by adding 20 c.c. of 95 percent alcohol to 2 grams of the pigment, heating to a boil, and allowing to settle. Pour off the alcohol, boil with water, and allow to settle, then use very dilute ammonium hydroxide. If either the alcohol, water, or ammonium hydroxide is colored, it indicates organic coloring matter. The quantitative determination of such adulteration is difficult and must generally be estimated by difference."

VERMILION.

"True vermilion, or, as it is generally called, English vermilion, is sulphide of mercury. On account of its cost it is rarely used in paints, and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with carbon disulphide. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1 percent. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. Ash in a muffle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury; but if this is required it may be determined by mixing 0.2 gram of the vermilion with 0.1 gram of very fine iron filings, or better 'iron by hydrogen.' Mix in a porcelain crucible and cover with a layer 10 mm. thick of the iron filings, place the crucible in a hole in an asbestos sheet so that it goes about half way through, cover with a weighed, well fitting, gold lid which is hollow at the top, fill this cavity with water, heat the crucible for fifteen minutes with a small flame, keep the cover filled with water, cool, remove the cover, dry for three minutes at 100° C., and thirty minutes in a desiccator, and weigh. The increase in weight is due to mercury. The mercury can be driven off from the gold by heating to about 450° C. A silver lid may be used, but gold is much better.

"It is well also to try the action of reducing and oxidizing agents such as stannous chloride, ferric chloride, etc. (See Zerr, Bestimmung von Teerfarbstoffen in Farblacken; also Schulz and Julius, A. Systematic Survey of the Organic Coloring Materials.)

"Paranitraniline red is soluble in chloroform. It is also well to try the solvent action on different reds, of sodium carbonate, etc. The amount of organic pigment present in such reds is generally very small, and when it cannot be determined by ignition to the presence of lead, zinc, or carbonate, it is best determined by difference."

BLUE PIGMENTS.

The only two blue pigments which come into great use in the paint trade are ultramarine and Prussian blue.

ULTRAMARINE BLUE.

Ultramarine blue is formed by burning together silicates, aluminates, sulphur, charcoal, and soda. Although of indefinite composition, it is essentially a silicate and sulphide of sodium and aluminum. This compound may be identified by its evolution of hydrogen sulphide when treated with acid. Although seldom used in the paint trade, if an analysis is desired, it may be carried out in the following way:

Moisture.—Heat 2 grams of the sample at 105° C. for two hours. The loss will be moisture.

Silica.—One gram of the sample is digested with 20 c.c. dilute hydrochloric acid to complete decomposition, taking care to avoid spattering. Evaporate to dryness, dehydrate, cool, moisten with a few drops of concentrated hydrochloric acid. Repeat the evaporation and dehydration, cool, moisten with a few c.c. concentrated hydrochloric acid, dilute with hot water, filter, and weigh the insoluble residue. Treat the contents of the crucible with an excess of hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness and ignite. The loss will be silica. Any residue remaining after this treatment should be examined.

Alumina.—The filtrate from the silica is treated with ammonium hydroxide until faintly alkaline. The aluminum hydroxide precipitated is filtered, washed, and weighed as Al_2O_3. If iron is present it may be separated from alumina by the fusion method as stated under the analysis of white pigments.

Sodium Oxide.—Treat the filtrate after the removal of the aluminum with sulphuric acid until faintly acid. Evaporate to dryness, weigh the sodium sulphate in a weighed dish. Should calcium be present, the sodium is determined in the filtrate after the removal and determination of the calcium as oxilate, in the way previously stated.

Total Sulphur.—One gram of the sample is fused with a mixture of potassium nitrate and sodium carbonate. Dissolve the fused mass in hydrochloric acid and boil, after the addition of concentrated nitric acid. Filter off the insoluble residue. Determine the sulphate in the filtrate in the usual way, by precipitation as barium sulphate with barium chloride. The sodium peroxide method for the oxidation of sulphur is often used for this determination.

Sulphur Present as Sulphate.—One gram of the sample is boiled with dilute hydrochloric acid until all the hydrogen sulphide has been driven off. Filter and wash the insoluble residue with hot water, precipitate the sulphur present in the filtrate, as usual. The amount of the sulphate present is deducted from the total sulphur found as sulphate by the fusion method, the difference calculated to sulphur and reported as such.

Ultramarine blues usually vary between the following limits:

Sulphur	10 to 14 per cent
Sulphur trioxide	2 to 5 per cent
Alumina	20 to 27 per cent
Silica	39 to 45 per cent
Soda	15 to 20 per cent.

PRUSSIAN BLUE (ANTWERP BLUE AND CHINESE BLUE)

This pigment is a double iron and potassium salt of hydroferricyanic and hydroferrocyanic acids. Its composition is rather indefinite and consequently analyses of the compound give varied results. The following method of analyses has been found to be quite satisfactory:

Moisture.—Two grams of the sample are heated at 105° C. for two hours. The loss will be moisture. Less than 7 percent moisture should be present in dry Prussian blue.

Iron and Aluminum Oxides.—One gram of the sample is ignited at a low temperature until the last trace of blue has been decomposed. The ignition must be low, so as to prevent any iron from being rendered difficultly soluble in hydrochloric acid. After cooling, treat the mass with 25 c.c. hydrochloric acid 1:1 and digest for one hour. No residue will remain if a pure Prussian blue is being examined. In some instances a residue does remain after this treatment, due to the presence of inert bases upon which the blue has precipitated, such as barytes. Should such an insoluble residue be present, evaporate the solution to dryness, take up with hot water and dilute hydrochloric acid, boil, filter, wash, and weigh the insoluble residue. Examine this for silica, barium sulphate, and alumina.

The filtrate from the last treatment, or the original solution, should no insoluble matter be present, is divided into aliquot portions. One of these portions is made faintly acid with ammonium hydroxide and the combined aluminum and iron hydroxides formed filtered, washed and weighed in the usual way. The iron may be determined in the combined oxides by fusion with potassium acid sulphate and titration with potassium permanganate in the usual way. The filtrate should be examined for calcium present as calcium sulphate.

Nitrogen.—Nitrogen is determined by the Kjehdahl-Gunning method. (Described in article on Food Analysis.)

Commercial Method.—According to Parry and Coste, the percentage of Prussian blue can be determined with sufficient accuracy for commercial purposes by multiplying the percentage of nitrogen by 4.4 and the percentage of iron by 3.03. The iron in this case may be titrated directly after solution in hydrochloric acid.

Alkalies and Sulphuric Acid.—Alkaline salts are estimated in the filtrate after the removal of calcium, in the usual way. One of them only will usually be present. Calculate to metal then to sulphate, accounting for all the sulphuric acid as alkaline sulphate.

Sulphuric acid is determined in the other aliquot portion, by precipitation as barium sulphate in the usual way. It is calculated to alkaline sulphate.

YELLOW AND ORANGE PIGMENTS (AMERICAN VERMILION CHROME YELLOW, LEMON CHROME, AND ORANGE CHROME).

The above pigments, varying in color, always contain chromates. The light colored pigments usually contain lead sulphate or other insoluble lead compounds. The darker pigments sometimes contain basic lead chromate. It is advisable to treat the pigment with alcohol to determine the presence of any organic coloring matter. Pure chrome yellow should contain only lead chromate and insoluble lead compounds. These pigments are analyzed in the following way:

Moisture.—Heat 2 grams of the sample at 105° C. for two hours. Loss will be moisture.

Insoluble Residue.—One gram of the sample is treated with 25 c.c. concentrated hydrochloric acid, the solution boiled, during which a few drops of alcohol are added one at a time. Dilute to 100 c.c. with hot water, continue the boiling for ten minutes, filter, wash, weigh the insoluble residue. This residue is examined for silica, barium sulphate, and alumina.

Lead.—After neutralizing the greater portion of the acid present with ammonium hydroxide, after the removal of the insoluble residue, the solution is diluted to about 300 c.c. with water. Precipitate the lead completely with hydrogen sulphide, allow to settle, evaporate, wash with hydrogen sulphide water. Dissolve the lead sulphide in hot dilute nitric acid, add an excess of sulphuric acid, evaporate until heavy fumes of sulphuric acid are given off, cool, dilute with water, add an equal volume of alcohol, filter, determine the lead either volumetrically or gravimetrically, as given under White Lead.

Chromium.—The filtrate from the lead precipitate is boiled until all the hydrogen sulphide is expelled. Precipitate the chromium as chromium hydroxide with ammonium hydroxide, observing the usual precautions for preventing the precipitation of zinc. Filter, wash, and weigh as chromic oxide. Calculate to chromic anhydride.

Zinc.—Precipitate the zinc in the filtrate from the chromium precipitation, with hydrogen sulphide under pressure in a flask, filter, wash, ignite and weigh as oxide or redissolve the washed sulphide and determine the zinc volumetrically, as before outlined.

Calcium and Magnesium.—Determine the calcium and magnesium in the filtrate in the usual way.

Sulphuric Acid.—The combined sulphate is estimated by dissolving 1 gram of the sample in hydrochloric acid, removing the insoluble residue by filtration, precipitating as barium sulphate, in the usual way. The barium sulphate precipitated will be pure, providing the solution is kept dilute and hot, otherwise lead sulphate may be precipitated. Should the precipitate become contaminated, the sulphate is best determined by dissolving the barium sulphate in conc. sulphuric acid and filtering on asbestos in a Gooch crucible. Weigh the residual lead sulphate.

GREEN PIGMENTS.

(CHROME GREEN.)

The green pigments which are of most importance are those consisting of a mixture of Prussian blue and chrome yellow. Organic colors are sometimes used to give the pigments a bright tint. It is well to examine all green pigments for coloring matter by boiling with alcohol.

Owing to the various composition of greens, due to the method of manufacture, a chemical examination is attended with many difficulties, and in many cases is of small value in determining the true value of the green. The usual methods of color assay for strength, by mixing with a weighed portion of white-base pigment and observing the tint produced, should be made. The pigment should also be carefully examined by means of the microscope, so as to determine whether the green is a product made by precipitating the two pigments together or by mixing the blue and yellow pigments after separate precipitation. The former have the greater value. A good green will show the presence of green and blue particles but no yellow, while poor green will show yellow and blue particles mixed with green. Analysis of the green may be made in the following way:

Moisture.—Heat 2 grams of the sample at 105° C. for two hours. The loss will be moisture.

Insoluble Residue.—One gram of the sample is heated at a very low heat in a casserole until the blue color has been completely destroyed, keeping the temperature sufficiently low so as not to render any of the iron or lead chromates insoluble. Cool, add 30 c.c. of concentrated hydrochloric acid, boil until all the soluble constituents have passed into solution. This can be hastened by the addition of a few drops of alcohol added one at a time. Dilute with water, boil, filter, wash, and weigh the insoluble residue. This residue is then carefully examined for silica, barytes, and occasionally alumina in the manner given under the analysis of a white pigment.

Lead.—The excess of acid present in the filtrate from the insoluble residue is neutralized with ammonia until barely acid. Dilute to 300 c.c., allow to cool, and treat with hydrogen sulphide until the lead sulphide is completely precipitated. Allow the precipitate to settle, filter, wash, dissolve in nitric acid, determine the lead as described under the analysis of yellow pigments.

Iron, Alumina, and Chromium.—The filtrate from the lead precipitate is boiled until all the hydrogen sulphide has been expelled. Add a fw drops of nitric acid, boil for a few minutes to complete oxidation of the iron, precipitate the iron, alumina, and chromium as hydroxides with ammonium hydroxide. This precipitate is filtered off, washed, and dissolved in hydrochloric acid and made up to a definite volume. In one portion the iron, aluminum, and chromium hydroxides are precipitated with ammonium hydroxide, filtered, washed, and weighed together. Another portion is treated in a flask with an excess of potassium hydroxide and bromine water until the iron hydroxide has assumed its characteristic reddish brown color. Dilute with water, filter, and wash. Dissolve the iron hydroxide in hydrochloric acid and determine the iron in the solution either volumetrically or gravimetrically, as stated under the analysis of iron oxides. The filtrate from the iron precipitate is made acid with nitric acid, and the alumina precipitated and determined in the usual way by precipitation with ammonium hydroxide. Chromium is determined in the filtrate by reduction to a chromic salt with hydrochloric acid and alcohol, precipitated with ammonium hydroxide and weighed as oxide.

Calcium and Magnesium.—Calcium and magnesium are determined in the filtrate from the iron, alumina, and chromium precipitation.

Sulphuric Acid.—One gram of the sample, after ignition until the blue is completely decomposed, as before stated, is dissolved in 30 c.c. of concentrated hydrochloric acid, diluted with water, boiled, filtered and washed. Determine the barium sulphate in the usual way.

Nitrogen.—Nitrogen is determined as stated under the analysis of Prussian blue.

Interpretations of Results.—The Prussian blue present is determined by multiplying the iron found by 3.03 or the nitrogen found by 4.4. The sulphate is calculated to lead sulphate and calcium sulphate, should calcium be present, and the chromium to lead chromate.

BLACK PIGMENTS (BONE BLACK, DROP BLACK, IVORY BLACK, LAMPBLACK, MINERAL BLACK, GRAPHITE).

The usual black pigments are those consisting of carbon existing either in the crystalline form (graphite) or the amorphous form which includes all the many artificial carbon blacks. Many paints are made at the present time from coal-tar and asphaltic mixtures, and it is deemed advisable to treat of these, owing to many difficulties attending their analysis, under a separate chapter. For the analysis of simple black pigments the following method will be found to embrace all the essential points needed for their examination. An extraction of the black pigments should be made with ether to determine the presence of oil. If present, it may be determined gravimetrically in a fat extraction apparatus.

Moisture.—Dry 2 grams of the sample at 105° C. for two hours. Loss will be moisture.

Volatile Matter.—One gram of the sample is heated in a large covered crucible with a Bunsen burner for ten minutes. The loss will be volatile matter.

Ash.—Two grams of the sample are ignited at a bright red heat until the carbon has all been driven off. The residue will be ash. Should the black pigment consist of graphite, the ignition must be made with the aid of oxygen. Ignite until all the carbon is burned off and report as carbon. Should carbonates be present, the ash is mixed with a small amount of ammonium carbonate and again ignited and weighed. This will reconvert any carbonates which may have been converted to oxides on ignition.

Soluble Salts.—The ash from the above is boiled with concentrated hydrochloric acid, diluted with water, again boiled, filtered, and the insoluble residue weighed. Should it be desired, the insoluble residue may be examined for silica, barium sulphate, and alumina. The filtrate is examined for phosphoric acid, calcium, and magnesium.

DETERMINING THE BENZOL IN GAS.*

The Chemist's Committee of the Association of German Ironmasters reported that it was desirable that an exact method of determining benzol in gas should be worked out, since there was at present no such method available for the examination of coke oven gas. Most of the methods hitherto described have applied to the coal gas of gas works, which contains considerably more benzol than coke oven gas, and these methods are more suitable for scientific than for works laboratories, where the greater part of the work is carried out by untrained men. Further, gas works attach little importance to the continuous testing of the gas for benzol. By benzol in this connection is understood the total of the compounds of this group, including benzene, toluene, xylene, etc.

Methods of benzol determination may be divided into two groups—those applicable to small quantities (viz. 100 cc. to 10 litres of gas) and those applicable to 5 cubic feet or more. The method of inferring the benzol content from the specific gravity of the gas in included in the first group. It presupposes that the gas has a definite composition, and in practice is more tedious than other methods. Another method which requires but little gas is the absorptiometric method of Dennis and O'Neill, which has been improved by Ellen S. McCarty. Nickel nitrate, or nickel cyanide, is used for absorbing the benzol; but the method is not very suitable for coke oven works, because it depends on exact gas analysis, and because of the small proportion of benzol in coke oven gas. For instance, the benzol in the crude gas from Westphalian coal corresponds with about 1 per cent by volume, and in the extracted or washed gas to about 0.07 per cent. Using a measuring vessel of 100 cc. capacity 1 per cent on the benzol would correspond with 0.01 cc. of benzol vapor, and with ordinary laboratory apparatus it is impossible to work closer than to 0.05 cc. Thus the absorptiometric method would invoice an error of at least 10 per cent. As an extraction of 90 per cent of the total benzol is ordinarily guaranteed, it would be impossible to ascertain by such a method of analysis whether the guarantee was properly fulfilled.

A similar method of working is that of Bunte and Haber, in which benzene and ethylene vapor are determined by means of bromine water. The ethylene is brominated, and benzene is soluble in the product of bromination. The ethylene is estimated from the consumption of bromine ascertained by titration, and the benzene is found by difference. This method is quite good for coal gas from gas works, but for coke oven gas it does not give equally trustworthy results, since the heavy hydrocarbons do not total more than about 2.8 per cent.

The method of nitrating the benzene takes a middle position in regard to exactness. Harbeck and Lunge nitrate about 10 litres of gas and weigh the nitrobenzene after drying it at about 80° C. or over concentrated sulphuric acid. Losses are inevitable by this procedure, since nitro-benzene is readily volatile. If the drying is done in a vacuum the determination is too slow, and becomes of little value for works-control purposes. Pfeiffer nitrates in a separating funnel of about half-a-litre capacity, which volume, with washed gas from coke ovens, would yield only 0.025 gramme of nitro-benzene, which is too small a quantity for exact work. Sainte-Claire Deville separates the benzene from about one cubic meter (35.3 cubic feet) of gas by cooling it to —22° C. A disadvantage of this process is that the benzene is not completely extracted, as at this temperature 23.5 grammes of benzene remain in a cubic meter of gas. In crude coke-oven gas, however, about 4 grammes of benzene per cubic meter have to be determined and in the washed gas still less. Owing to the tension of benzene vapor at —22° C., and the difficulty of maintaining apparatus at that temperature for six or eight hours, this method is of comparatively little value. A method somewhat similar that has been proposed, is to saturate the gas with benzene vapor by passing it through a saturator containing benzene, and from the quantity of liquid benzene taken up, calculating the quantity of benzene vapor necessary for the saturation of the gas. Only ten litres of gas are used by this method, which is therefore not suitable for the work under consideration.

Müller has used a method of absorption with cooled paraffin oil, which Nowicki modified by altering the form of absorption vessel in order to secure better contact of the gas and absorbent. The author has studied this method and introduced a modification of the apparatus, which extends its range of application and makes it suitable for coke oven works. It is not necessary to use paraffin oil, as good results may be obtained with tar oil; but the freedom from color of paraffin oil is in its favor. The author determined the quantity of benzene absorbed by 50 cc. of oil in the washing flasks employed. He found that, when cooled to —18° C., 50 cc. of the following oils absorbed from gas the weight stated of benzene: Tar oil boiling between 170° to 205° C., 3.5 grammes; tar oil boiling between 240° to 270° C., 4.5 grammes; tar oil boiling between 260° to 340° C., 3.2 grammes; and paraffin oil boiling above 300° C., 4.6 grammes. In determination, however, these limits of absorption should never be attained. In the author's investigations more than 0.8 gramme of benzene was never absorbed in the first flask.

A point of practical importance in regard to the washing oil is that an oil which of itself yields much light oil on distillation contaminates the benzol distillate and makes it difficult to work-up, but this, of course, applies only to the first time of using the washing oil. The most suitable washing oil is one which yields at the most 10 per cent of distillate below 200° C., and at least 90 per cent of distillate below 300° C. The best tar oil for washing is one which distils between 240° and 260° C.

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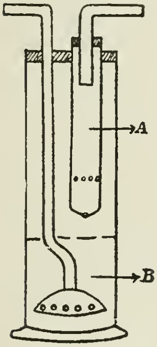
*From the American Gas Light Journal; an abstract translation in the London Journal of a paper by Dr. A. Krieger.

The author tried various forms of absorption apparatus, most of which allowed some of the oil to be carried forward by spurting or as spray. After many trials, he finally adopted the washing cylinder shown. This has a height of about 9 inches, and a diameter of 2 inches. It is charged with 50 cc. of the washing oil (*B*). The outlet tube (*A*), packed with glass beads about 1/12th inch in diameter, is 6 inches long and ½-inch diameter inside. There is a small hole in its bottom, and about ½-inch from the bottom is a ring of small holes for the inflow of the gas. This tube is closed by a cork, with glass outlet tube that connects it with the next cylinder. In use, mechanically sprayed oil is completely retained in this outlet tube, owing to the obstruction of the beads. Two absorption cylinders serve to absorb the benzol completely from the gas, though in the author's investigations three cylinders charged with oil and one packed with cotton wool were used. The cylinder containing cotton wool was used for many months without showing perceptible alteration in weight. Hence for practical purposes it was found that the third cylinder charged with oil and the one packed with cotton wool could be dispensed with. The first cylinder ordinarily absorbed about 0.8 gramme of the benzol, and the second cylinder not more than 0.05 gramme.



With a view to securing further simplification, experiments were tried with cooling and without the use of paraffin oil, and on the use of paraffin oil without cooling. In the one case the empty cylinders were cooled in ice at a temperature of about—18° C., and it was found that only a small proportion of the benzol was extracted from the gas. Working with paraffin oil without cooling gave a rather higher extraction; but a long series of experiments showed that both absorption and cooling are necessary to ensure the exact determination of the benzol in gas in a simple manner. A balance weighing to 0.01 gramme on a load of 3 kilogrammes is sufficiently accurate for the purpose, and the determination may be carried out by anyone capable of using the balance. In order to avoid errors due to the difference in weight of more or less air or gas in the cylinder, the air in it is displaced by dry gas before the first weighing; and after the absorption the cylinder is brought to the room temperature with one of its connections attached to a low pressure gas supply and the other connection closed—a drying tube being interposed between the gas supply and the cylinder. The weighings before and after absorption are then comparable. About 40 litres of gas are passed through the apparatus per hour; hence when determining the benzol in gas which has passed through oil washers on the works the test extends over about 8 hours.

It may be assumed that the process effects a determination of benzol in gas which is to all intents and purposes quantitative. When 5 litres of the washed and cooled gas was nitrated with a mixture of sulphuric and nitrate acid there was no smell of nitrobenzene. Bauer has shown that 0.4 volume of benzol vapor in 10,000 volumes of air can be detected on nitrating by the smell.

An objection to this method of determination is that it involves the use of ice, 2¼ pounds of ice being necessary for one determination. The process, as described, makes it possible to determine benzol in quantities of only 2 grammes per cubic meter (874 grains per 1,000 cubic feet) of gas. The method is sufficiently simple and convenient for use in works control, and as the recovery of benzene and its homologues (toluene, etc.) from gas is now becoming a matter of considerable importance, such a method of determination is likely to be of service in securing good results from the washing plant.

Rubber Manufacturers and the Brazilian Tariff.

The Brazilian budget law provided for certain surtaxes on manufactures of rubber when made of rubber of other than Brazilian origin, and for certain other customs duties intended to favor the increased use of Brazilian rubber. The enforcement of the new requirements was suspended until April 1, but, according to a telegram received April 6, 1915, from the American consul general at Rio de Janeiro, they are now in force. To obtain exemption from the surtaxes it is necessary to furnish a certificate to the effect that Brazilian rubber—"fine Para," according to the law—has been used in the manufacture of the rubber goods imported. No regulations have been issued for the application of the new law, and it is reported that the collectors are experiencing some difficulty in enforcing it. The importers have protested, and it is not unlikely that the matter will be reconsidered at the session of the Brazilian Congress which convenes in May. A full statement of the changes provided for in the budget law will be contained in a note to be published shortly in Commerce Reports. Rubber goods from the United States are entitled to a reduction of 20 per cent of the regular customs duties in Brazil.

A Commerce Report of June 12 states that over 20,000 tons of potash salts, the property of American firms, purchased before the recent embargo on German exports, are now interned on three steamers in German ports.

METALLURGY

OXYGEN IN STEEL.*

By J. A. PICKARD AND F. M. POTTER.

The following work was undertaken as part of a systematic examination of the oxygen content of commercial steels with a view to collecting trustworthy evidence as to the amount of oxygen normally to be expected in good class material, and the limits within which it is desirable to restrict this element.

The method of estimation, which consists in heating the steel in a confined volume of hydrogen with a weighed boat containing phosphorus pentoxide and measuring the increase in weight of the boat, has been used throughout and has fully confirmed the opinion arrived at as to its convenience and reliability. The determinations were in most cases carried out in duplicate by the two authors independently.

All the steels examined were made by either the acid or the basic open-hearth process, and, as far as can be judged from the analyses, they were generally of excellent quality. In the following tables the samples are arranged in order of carbon content. The actual figures obtained for oxygen in duplicate analyses are given in the last two columns, and show the amount of agreement ordinarily obtained when using this method. Six of the results are reprinted from the former paper (Carnegie Scholarship Memoirs, 1913, page 70) and are included here for ease in reference.

CONSIDERATION OF RESULTS.

It had been expected from the results published in a former paper that it might be possible to discover some relationship between the oxygen and the carbon content, but the results quoted lend but little support to this theory. Samples 9 and 12, containing 0.14 and 0.26 percent of carbon respectively, contain only 0.011 and 0.005 percent of oxygen, while No. 14 with 0.32 percent of carbon contains 0.041 percent, and even No. 22 with 0.61 percent of carbon also contains 0.041 percent of oxygen. One most important conclusion to be drawn is that it is possible to make all kinds of open-hearth steel, even low-carbon low-silicon basic (No. 9), practically free from oxygen—containing only 0.010 percent or under. That some steels are made containing more than that amount is, however, abundantly shown by the other results, and it is to be observed that the cheaper steels contain higher oxygen.

Acid open-hearth steel is generally admitted to be of better quality than basic open-hearth, and it has been suggested that this is due to the higher oxygen content in basic steel. In the foregoing tables all the high-oxygen steels (that is, over 0.020 percent) except one (No. 2) are found in the basic group, so that the evidence does support the conclusion that basic steel is higher in oxygen. It is to be noted, however, that only two of the basic steels are higher in carbon than the lowest of the acid group, and no marked difference is to be noted in those samples comparable in carbon content; indeed No. 2, an acid steel, is higher in oxygen than Nos. 23, 25 and 26, which are basic.

An interesting question is raised by the fact that the samples that must have received most hot-working are all high in oxygen. Nos. 14 and 15 were taken from two fishplates, No. 22 from a rail, while the other samples were from fair-sized billets. The possibility that the oxygen content may vary after the steel has solidified has, so far as the authors are aware, not

TABLE I.—ACID OPEN-HEARTH STEEL.

Sample.	Carbon, per cent.	Manganese, per cent.	Silicon, per cent.	Sulphur, per cent.	Phosphorus, per cent.	Oxygen, per cent.		
1	0.67	0.73	0.95	0.035	0.027	0.004	0.004	Mean— C., 0.87 O., 0.011
2	0.79	0.65	0.210	0.030	0.050	0.020	0.021	
3	0.93	0.68	0.035	0.031	0.027	0.007	0.006	
4	1.08	0.62	0.024	0.033	0.022	0.012	0.016	
5	1.18	0.65	0.056	0.027	0.025	0.005	0.006	Mean— C., 1.35 O., 0.007
6	1.33	0.42	0.140	0.030	0.024	0.004	0.007	
7	1.55	0.49	0.100	0.027	0.026	0.010	0.012	Mean of all— O., 0.0096

TABLE II.—BASIC OPEN-HEARTH STEEL.

Sample.	Carbon, per cent.	Manganese, per cent.	Silicon, per cent.	Sulphur, per cent.	Phosphorus, per cent.	Oxygen, per cent.		
8	0.10	....	.....	.....	.....	0.038	0.036	
9	0.14	0.35	0.020	0.033	0.018	0.010	0.011	
10	0.20	....	.....	.....	.....	0.031	0.028	
11	0.23	0.70	.....	0.060	0.026	0.013	0.014	Mean— C., 0.25 O., 0.021
12	0.26	0.49	0.120	0.030	0.031	0.003	0.006	
13	0.30	....	.....	.....	.....	0.030	0.027	
14	0.32	0.62	.....	0.051	0.020	0.040	0.041	
15	0.33	0.62	.....	0.057	0.025	0.024	0.021	
16	0.35	0.56	0.182	0.027	0.020	0.005	0.008	
17	0.41	0.52	0.026	0.032	0.023	0.019	0.014	
18	0.44	....	.....	.....	.....	0.029	0.025	
19	0.54	0.69	0.085	0.022	0.024	0.003	0.003	Mean— C., 0.52 O., 0.021
20	0.55	0.97	.....	0.055	0.011	0.016	0.017	
21	0.55	....	.....	.....	.....	0.020	0.020	
22	0.61	0.74	.....	0.053	0.021	0.038	0.044	
23	0.66	0.65	0.100	0.033	0.052	0.005	0.006	Mean— C., 0.81 O., 0.011
24	0.75	0.38	0.025	0.025	0.022	0.025	0.026	
25	0.82	0.67	0.096	0.030	0.028	0.004	0.007	
26	1.00	0.67	0.036	0.016	0.025	0.006	0.007	Mean of all— O., 0.0189

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*From The Iron Age, the material being taken from a paper prepared for the abandoned fall meeting in Paris of the Iron and Steel Institute.

hitherto been considered. It must be borne in mind, however, that these steels, as judged from their other constituents, were not of the very highest quality, and that Nos. 8, 10, 13, 18 and 21, which are all high in oxygen, were of cheap make. It is hoped to investigate the influence of hot-working on the oxygen content in a subsequent paper.

THE DETERMINATION OF CHROMIUM AND MANGANESE IN IRON AND STEEL.*

By FRED C. T. DANIELS.

In steel furnace operations it is frequently necessary to include chromium among elements to be determined in the preliminary analysis. The following 20-minute method has been worked out to fill this necessity. It has been in constant use for the past two years and is sufficiently accurate to be used as a daily routine method, and it occupies but little of the chemist's actual working time.

The method for chromium is an adaptation of the persulphate method for the manganese determination in iron and steel.

The method for managanese is the persulphate method except that the sum of the manganese and and chromium is obtained in this titration and the manganese calculated by difference, using the results from the chromium determination. The objection to the usual persulphate method for manganese, in the presence of chromium, is that a varying quantity of the chromium is reduced along with the manganese by the ferrous ammonium sulphate or sodium arsenite. If determined colorimetrically, the chromium gives the solution a different shade, which is difficult to compare. This may be overcome by using for a standard a steel containing approximately the same amount of chromium as the sample. A still more convenient way is to add the chromium as potassium bichromate, using a standard solution so that 1 cc. would equal 0.0005 gram of chromium, *i. e.*, 0.25 per cent chromium for a 0.20 gram charge of the sample. This solution is added to the standard after the solutions have been transferred to the color comparison tubes.

Chromium—Weigh 1 gram of the sample into a 300 cc. Erlenmeyer flask (Jena glass), add 100 cc. nitric acid (1.135 specific gravity), place on the hot plate, and when solution is complete, boil off all nitrous fumes. (The volume of the solution should not be less than 75 cc. It is unnecessary to filter off the silicon and graphite residue if the solution is complete. When the sample is high in combined carbon, it is well to add a few crystals of ammonium persulphate when the solution is complete and boil a moment longer to destroy the combined carbon). Remove the flask from the hot plate, add 75 cc. silver nitrate solution (2.00 grams per liter, and immediately 5 grams of ammonium persulphate crystals. Replace flask on the hot plate and bring gently to boiling. Boil vigorously for a minute, and while still boiling add dilute hydrochloric acid, drop by drop, until the permanganate color is completely destroyed. Continue the boiling for one minute and then cool the flask immediately in water. Titrate by adding an excess of tenth-normal ferrous ammonium sulphate solution above that required to reduce the chromium, and titrate back with tenth-normal potassium permanganate solution. The number of cubic centimeters of the ferrous ammonium sulphate oxidized by the chromate, multiplied by 0.00174, gives the weight of chromium in the sample.

Manganese in the Presence of Chromium—Proceed according to the above directions for the determination of chromium except that after the ammonium persulphate is added, only heat until the solution just comes to boiling, then cool immediately and titrate as before, this time adding enough ferrous ammonium sulphate to reduce both the manganese and chromium. The number of cubic centimeters of ferrous ammonium sulphate used, minus the number used in the chromium determination, multiplied by 0.0055, equals the weight of manganese in the sample.

The ultimate value of the solutions may be used in calculations as above. In this case it is advisable to carry along a blank with a sample containing no chromium and subtracting the blank. The standardization of the solutions against a standard steel is the most satisfactory procedure.

OIL MILLING IN JAPAN.

According to the Japan Mail of Jan. 11, one of the few lines of industry which has been favorably influenced by the war is seed oil milling. On account of the withdrawal of Germans, because of the war, the laying in of beans in China has become very easy for the Japanese in China. Particularly the decline of prices has offered to them a vast chance of underselling even Russian millers in their own country, while the demand for various descriptions of vegetable oil has been inflated both at home and abroad, due to the increased requirements of the navies of the different countries. Though at one time the trade with Europe was suspended at the fall of Antwerp, soon the trade was resuscitated and now is unusually active. The only drawback is the inadequacy of shipping to take the goods to the consuming countries.

The industry in this country may be divided into three lines, namely, seed oil milling in and around Nagoya, rape-seed oil milling principally conducted in Kyushu, and Chinese bean and seed oil milling conducted in and around Kobe. Millers engaged in the former two lines have never been favored by the war, for they have been unable to obtain cheap materials, which in their cases are home produced. Moreover, they have been faced with a decrease in the demand for cakes from farmers on account of the cheapening of rice. It is the last line which has been most favored by the war.

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*From the Journal of Industrial and Engineering Chemistry.

THE TESTING OF ORES FOR THE CYANIDE PROCESS.*

By WELTON J. CROOK.

ACIDITY.

Solutions of the alkaline cyanides are very easily decomposed by a multitude of substances and under many conditions. The hydrocyanic acid resulting from these decompositions is but sparingly soluble in water and if the solution contains dissolved salts, its solubility tends to be decreased. Hydrocyanic acid contains the active and useful elements which enter into the reactions which make the cyanide process possible and these are lost by the volatilization of the acid.

Among the substances which tend to decompose solutions of the alkaline cyanides, are the mineral acids and their salts; the common ones being H_2SO_4, H_2CO_3, HCl, HNO_3, $FeSO_4$, $Fe_2\ (SO_4)_3$, $CaSO_4$, etc. Wood, jute and cocoa fibre (when new) also have the same effect, lastly, the sulphides of iron and copper, especially if partly decomposed by weathering, are very active as decomposing agents. These groups of substances are called "cyanicides" and may be defined as "Substances which decompose active cyanides, forming compounds which are not solvents of gold and silver." Many of these substances may be neutralized by the presence of soluble alkalies and the term "Acidity" as used in ore testing, includes acids and salts which may be so neutralized.

Acidity may be readily divided into two classes: (a) Soluble acidity, and (b) Latent acidity. Soluble acidity is the acidity caused by soluble acids and salts soluble in water, while latent acidity is that caused by salts and substances not soluble in water but which, nevertheless, are able to decompose alkalies. Latent acidity is largely due to the presence in the ore of certain basic salts and to the presence of undecomposed sulphides.

"Total" acidity includes the sum of both soluble and latent acidity.

In the treatment of ores having a very high soluble acidity, preliminary water washes may be employed with advantage and this is especially the case in treating weathered tailings containing iron and copper sulphides. It is then possible to remove, if necessary, a large part of the soluble acidity, so that the use of the added alkali is principally to overcome latent acidity. The substance which causes latent acidity decomposes cyanide but slowly and will react with any free alkali which may be present, in preference to the alkali cyanide. It may therefore be said that alkali protects cyanide, hence the term "protective" alkalinity.

In the early day of the history of the cyanide practice, much difference of opinion existed as to the best alkali to use as a neutralizing agent for acidity. Caustic soda and lime were the most generally considered. Lime has several advantages in practice among which are its cheapness, slow solubility and the fact that 1 pound of lime is as effective as 1.4 pounds of caustic soda also to the fact that it has great power of coagulating and settling slimes and turbid water.

However, in making laboratory tests for acidity, lime is not as suitable a reagent as sodium or potassium hydroxide on account of its slow and slight solubility in water. In the tests outlined, sodium or potassium hydroxide is accordingly used and from the results obtained, the equivalent amounts of lime are calculated. It will be shown further on in this article how this calculation may be made.

In making the acidity tests it is necessary to have two standard solutions, one an acid and one an alkali. It is most convenient to have them of equal strength, that is to say, one c.c. of acid exactly equalling one c.c. of alkali when titrated against each other using phenolphthalein as an indicator.

The most convenient standard acid solution to use for this purpose is that of oxalic acid, as this may be standardized by weighing out the solid acid, and because it is also used in determining available calcium oxide in lime as will be shown in the next installment of this article. In this way it is readily possible to make a comparison between the standard solution of caustic alkali and the lime which will be used in subsequent tests on the ore.

It may be objected that a standard oxalic acid solution prepared by weighing the solid acid is not accurate owing to the uncertain hydration of the crystals, but it has been found that if the acid used is fresh and has been preserved in a carefully stoppered bottle, the results obtained will be easily accurate enough for this use.

The standard acid solution is prepared by weighing out 14.6068 grams of oxalic acid and dissolving in 1 litre of distilled water. The reason for using acid of this strength is as follows: The number of grams of ore used in the acidity tests is calculated from the strength of the acid, but in order to simplify the explanation it is assumed that the weight of ore is known and the strength of acid unknown.

If lime is added at the rate of 1 lb. per ton of ore, then 1-2000 or 0.0005 times the weight of ore, in lime, is added for each pound per ton required. In making the tests, 26 grams of ore are agitated with 100 c.c. of water and then filtered, the acidity in 50 c.c. of the filtrate is then neutralized with the standard alkali solution. The 50 c.c. titrated contains the acidity from 13 grams of ore. $13 \times 0.0005 = 0.0065$ grams of lime to be added to 13 grams of ore for each pound of lime required.

The combination of lime with oxalic acid is represented by the following equation:

$$H_2C_2O_4,\ 2H2O + CaO = CaC_2O_4 + 3H_2O.$$

From which it is seen that 126 parts by weight of oxalic acid reacts with 56 parts by weight of CaO. Therefore the weight of oxalic acid which combines with 0.0065 grams of CaO in found by the proportion:

$$0.0065 : 56 :: x : 126 \qquad x = 0.0146068$$

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*From the Pahasapa Quarterly.

Therefore 0.0146068 grams of acid are to be contained in each c.c. of solution if each c.c. is to represent a pound per ton of lime to be added. 0.0146068 × 1000 = 14.6068 grams of oxalic acid to be added to 1 litre of water to make the standard solution.

A standard alkali solution of equal strength to the standard acid may be prepared as follows: The reaction between oxalic acid and caustic soda is represented by:

$$H_2C_2O_4, 2H2O + 2NaOH = Na_2C_2O_4 + 3H_2O.$$

In which 126 parts of oxalic acid neutralize 80 parts of sodium hydroxide. The weight of sodium hydroxide which should be contained in a litre of standard alkali is found therefore from the proportion:

$$126:80::14.6068:x \quad x = 9.274$$

In weighing out the NaOH (which is seldom pure) it is best to take say 9.3 grams and dissolve in 900 c.c. of distilled water, making preliminary titrations against standard acid and calculating the dilution necessary. This calculation sometimes seems to give trouble to those unfamiliar with such work, so an example will be worked out.

Suppose that it was found that 10 c.c. of the alkali solution required 11.2 c.c. of the standard acid. Then for each 10 c.c. of the alkali remaining of the 900 c.c. there must be added 1.2 c.c. of water. There remains 900 — 10 or 890 c.c. The water to be added therefore equals 890 ÷ 10 × 1.2 or 106.8 c.c. The alkali solution, if kept in a well stoppered bottle, will vary but little.

TO DETERMINE SOLUBLE ACIDITY.

Place 26 grams of ore (ground to 100 mesh) in a clean, dry agitator bottle with 100 c.c. of distilled water and agitate for from one-half to one hour. Allow to settle for a few minutes, then decant the clear supernatant liquid into a filter and collect the filtrate in a clean, dry beaker. (Do not wash the residue or otherwise dilute the filtrate.) Measure 50 c.c. of the filtrate into an Erlenmeyer flask, add a few drops of phenolphthalein and titrate with the standard alkali solution.

Care must be taken not to over titrate because the amount of soluble acidity in most ores is very small. If, however, this is done, the solution may be titrated back with the standard acid. The number of c.c. alkali used measures the amount of soluble acidity.

TO DETERMINE THE TOTAL ACIDITY.

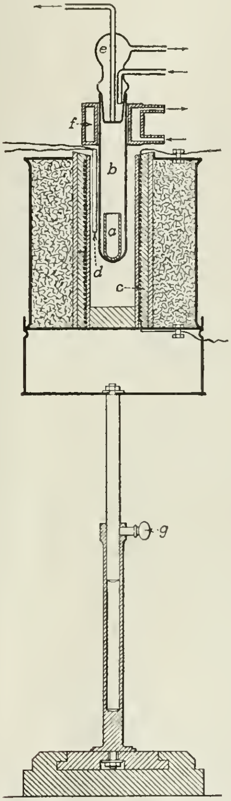
Place 26 grams of ore (100 mesh) in a clean agitator bottle with 100 c.c. of standard alkali solution. Agitate for at least 6 hours. Allow to settle, decant the clear liquid into a filter and collect filtrate in a clean, dry beaker. Titrate 50 c.c. of the filtrate with the standard acid solution.

Fifty c.c. minus the number of c.c. of standard acid used equals the number of c.c. of standard alkali neutralized by the total acidity of the ore, and hence the number of pounds of lime to be added per ton.

The latest acidity is found by subtracting the soluble acidity from the total acidity.

A METHOD FOR DETERMINING GASES IN STEEL.*

A new method of determining the gases in iron or steel has recently been published in Germany by P. Goerens and J. Paquet in Ferrum, a German journal devoted to technical progress in the iron and steel industry. The article, entitled "Ueber Eine Neue Methode zur Bestimmung der Gase im Eisen," goes into every detail of the apparatus, its manipulation and the results achieved and covers the determination of carbon dioxide, carbon monoxide, hydrogen and nitrogen. An abstract follows:



Apparatus for Melting Steel With Iron and Antimony.

If chips of iron are heated in a vacuum a mixture of CO_2, CO, H and N is given off. The quantity of the gases depends on the conditions under which thee experiment is carried out, being influenced by the degree and length of the heating as well as by the character and form of the material tested. Previous methods of determining the gases rest almost entirely on heating the metal in a vacuum. The results are comparable only when obtained under similar conditions. But by all these methods the total quantity of gas cannot be obtained. A new method is here described which endeavors to remove the principal objections to previous ones.

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*From The Iron Age.

The principle of the new method consists in melting in a vacuum the metal to be tested with tin and antimony to a thin fluid alloy and analyzing the gases thus released. The apparatus consists of three parts: The melting apparatus, the air pump and the analyzing apparatus. The melting of the material to be tested is done by electrically controlled heat in a magnesia crucible, the gas contents of which have been carefully removed.

The illustration shows the melting device. The magnesia crucible *a*, with its mixture of the sample and the tip and antimony is put into a thick-walled reagent tube, *b*, made of molten rock crystal, which is heated to the required temperature by means of an electric resistance furnace, *c*. The temperature is controlled by means of a thermoelement, *d*, inserted between the tube containing the crucible and the wall of the electric oven. The closing of the reagent tube is accomplished by means of a water-cooled stopper, *e*, which is also made of molten rock crystal. To prevent a heating up of the stopper as well as to furnish a support for the tube, a water-cooled brass ring, *f*, is supplied. The furnace, *c*, can be raised or lowered by means of the arrangement at *g*.

The selection of a sample is especially important as gases are not uniformly distributed in steel as iron. In order to obtain an average sample it is better to plane or mill a complete cross section, care being taken that no traces of oil or moisture are absorbed. The sample is mixed with a corresponding quantity of antimony and tin, the Kahlbaum products being recommended as having negligible amounts of gas in them, and then placed in the magnesia crucible.

Commenting on the results of the method, the authors say:

Of the different gases which are determined by this method, the larger part is given off during the melting while the mechanically held oxides react with the constantly present carbon to form CO_2 and CO. On the other hand CO_2 and CO react with the metal as well as with the carbon. Therefore it is impossible to separate the gases actually in the metal from those which result from these reactions. For judging the material, therefore, it suffices to establish the total quantity of gas independent of its origin. It is, in fact, clear that a poorly deoxidized steel, in which, besides the carbon, there is an appreciable amount of oxides which can react to form oxides of carbon, is of poorer quality than a steel well deoxidized which contains less gas. It has been shown that well-deoxidized material such as electric steel has a smaller quantity of gas than ordinary steels.

Another difficulty arises in connection with the information furnished by the analyses. It is known that a mixture of CO_2 and CO in conjunction with carbon changes its composition with the temperature. These changes follow the tendency that by lower temperature mixtures ensue rich in CO_2, so that it cannot be definitely stated whether the CO_2 found by the analysis

TABLE SHOWING THE GAS CONTENTS AND COMPOSITION OF VARIOUS GRADES OF STEEL DETERMINED BY THE NEW METHOD.

Sample.	Carbon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulphur, per cent.	Silicon, per cent.	Nickel, per cent.	Chromium, per cent.	Gas in cu. cm. per 100 g. metal.	Carbon dioxide, CO_2, per cent.	Carbon monoxide, CO, per cent.	Hydrogen, per cent.	Nitrogen, per cent.	Total gas, per cent.
Basic Bessemer ingots—													
1	0.05	0.36	0.110	0.045	....	...	...	22	0.0040	0.0196	0.0003	0.0029	0.0268
2	0.08	0.40	0.080	0.048	....	...	...	40	0.0090	0.0352	0.0006	0.0025	0.0383
3	0.05	...	0.080	0.040	....	...	...	41	0.0077	0.0342	0.0006	0.0065	0.0413
4	0.05	0.40	0.080	0.040	....	...	...	49	0.0061	0.0393	0.0006	0.0122	0.0521
Open-hearth ingots—													
5	0.08	0.40	0.050	0.030	....	...	...	38	0.0048	0.0341	0.0005	0.0061	0.0455
6	0.15	0.37	0.060	0.060	....	...	...	46	0.0048	0.0410	0.0009	0.0024	0.0443
7	0.08	0.44	0.040	0.037	....	...	...	78	0.0178	0.0785	0.0007	0.0020	0.0812
Electric steel—													
8	0.19	0.50	0.020	0.012	0.420	...	...	10	0.0047	0.0061	0.0002	0.0015	0.0125
9	0.08	0.35	0.010	0.010	0.090	4.34	1.10	13	0.0082	0.0015	0.0007	0.0000	0.0104
10	0.10	0.38	0.011	0.010	0.070	3.30	...	15	0.0064	0.0061	0.0007	0.0000	0.0132
11	0.15	0.49	0.011	0.012	0.450	...	...	25	0.0058	0.0092	0.0012	0.0048	0.0210
12	0.26	0.43	0.068	0.023	0.015	...	...	25	0.0053	0.0098	0.0012	0.0041	0.0214
13	0.10	0.40	0.010	0.012	0.100	...	...	28	0.0053	0.0207	0.0008	0.0019	0.0287
14	0.45	0.38	0.018	0.022	1.270	...	...	32	0.0058	0.0167	0.0013	0.0042	0.0280
15	0.98	0.45	0.158	0.075	0.015	...	...	70	0.0043	0.0688	0.0010	0.0083	0.0824
16	0.71	0.37	0.018	0.016	0.230	...	...	73	0.0106	0.0684	0.0010	0.0078	0.0878
17	1.35	0.44	0.020	0.015	0.190	...	0.37	88	0.0053	0.0851	0.0010	0.0141	0.1055
18	0.10	0.35	0.009	0.008	0.170	3.62	0.90	94	0.0018	0.0569	0.0047	0.0012	0.0646
19	1.16	0.38	0.017	0.016	0.180	...	...	94	0.0050	0.0900	0.0011	0.0124	0.1085
20	0.33	0.38	0.026	0.016	0.100	3.06	1.94	105	0.0109	0.0708	0.0039	0.0056	0.0912
Crucible steel—						Ni.	Wo.						
21	0.38	0.26	0.056	0.021	0.190	...	0.65	29	0.0090	0.0248	0.0004	0.0024	0.0366
22	0.84	0.36	0.041	0.017	0.150	...	...	41	0.0058	0.0391	0.0007	0.0015	0.0471
							Cr.						
23	0.16	0.14	0.008	0.008	0.290	4.00	0.91	50	0.0032	0.0271	0.0022	0.0053	0.0378
24	0.47	...	0.020	0.028	....	2.98	1.29	51	0.0200	0.0257	0.0016	0.0068	0.0541
25	0.97	0.14	....	0.010	0.120	...	...	79	0.0098	0.0712	0.0017	0.0020	0.0847
26	0.27	0.45	0.010	0.012	0.240	4.00	1.30	152	0.0096	0.1290	0.0041	0.0082	0.1509

was really in the metal or was formed by decomposition of the CO. It would be expedient, perhaps, to calculate the CO_2 found to CO under the assumption that the CO_2 found arose from the decomposition of the CO. According to the researches of Goutal the presence of CO_2 in iron at ordinary temperatures is denied.

The results by this method of various analyses of different kinds of steel are given in the table. The total gas content is expressed in cubic centimeters per 100 grams while the various gases are reported in percentage by weight. Commenting on these results the authors say:

Total Gas Content.—The lowest total gas content was found in low carbon electric steel, well deoxidized material showing 10 to 15 cu. cm. of gas per 100 grams of metal. High carbon electric steel contains in general more gas, but this is not proportional to the carbon content. In badly deoxidized electric steel the gas content rises to tenfold, as shown by samples 18 and 20. Bessemer and open-hearth steel show average gas contents of 22 to 78 cu. cm. per 100 grams.

Oxides of Carbon.—The CO_2 varies from 0.0020 to 0.0200 per cent by weight, but as the amount depends on the method of conducting the analysis, the figures do not offer a sure account of the actual CO_2 present. The CO ranges from 0.0015 to over 0.1000 per cent in sample 26. High content of CO is generally a proof that deoxidation was not complete. In a carefully manufactured nickel-chrome steel, sample No. 9, the CO content is 0.0015 per cent. It is customary to add ferro silicon to modify the percentage of CO, yet in this sample with 0.10 per cent silicon present, the steel is not free from CO. Also in sample No. 18 of similar composition nearly 40 times as much CO is present with a percentage of silicon of 0.17. In the crucible steels, where 0.12 to 0.24 per cent of silicon is present, the presence of this gas is by no means low.

Hydrogen.—The hydrogen ranges from 0.0002 to 0.0047 per cent. Carefully prepared, well deoxidized ingot steel contains as a rule but little hydrogen. Ferromanganese often contains considerable hydrogen which adds to the amount in the final steel.

Nitrogen.—The content of nitrogen varies between nothing and 0.0141 per cent, being particularly low in the electric steels.

The article also contains a detailed discussion of the relation of the gases and their proportion in the different stages of steel manufacture by different processes, as well as in the refinement of open-hearth steel in the electric furnace. The results are displayed both by charts and by tables and are decidedly interesting and thorough.

FILTERING PRODUCER GAS.*

The use of producer gas in the place of natural gas, increasing in some of the iron and steel districts, carries with it the necessity of guarding against the sulphur content of the gas used. Concerning the unfavorable effect upon the quality of the steel produced in the gas-fired, open-hearth furnaces, "it is perfectly clear," says a leading authority, "that some sulphur is absorbed from this gas in the steel, and much steel is injured for some purposes in the effort to reduce the sulphur. If the sulphur could be eliminated from the producer gas, it would meet the needs of the case much better than to remove the sulphur afterwards from the steel."

The object of this paper is to bring to the attention of steel manufacturers a very simple but entirely effective means of purifying producer gas which was first observed by the writer in Germany and has since been followed up in this country. The system provides, in brief, for placing, between the producers and the furnaces, a filter plant of sufficient capacity to remove all traces of sulphur. The filter boxes are built up of successive layers, on racks, of iron oxides. The material originally used abroad was bog iron, and this served the purpose, in a measure, as long as enough filtering surface was presented. But there are now available at commercial rates, both in this country and Europe, especially prepared iron oxides, known under various trade names, which are positive in their purifying action and have several times the efficiency of bog iron.

CHEAPER COAL MADE AVAILABLE.

Before taking up the producers and filters, however, there is the matter of coal to be considered; and one of the most important features of the system is the fact that it enables a much less expensive grade of coal to be used for the producers.

The sulphur content of gas is naturally a percentage of the sulphur in the coal from which the gas is made. Under present conditions, therefore, the quality of the coal is of much importance to the open hearth steel manufacturer whose reheating pits and furnaces are fired with producer gas; and he must either continue to buy low-sulphur coal at a premium or else find some inexpensive means of gas purification.

In general, about 40 percent of the sulphur in coal passes into the gas produced from it. A long ton of ordinary Westmoreland coal of average quality makes about 10,750 cu. ft. of gas. If this coal contains 1.5 percent sulphur, we have, therefore, 0.6 percent or 13.44 lbs. of sulphur leaving the producer for each ton of coal. A portion of this is taken out in the mechanical processes of washing and scrubbing, leaving say 11 lbs. of sulphur, or about 720 grains per cu. ft., to pass on with the gas into the furnaces.

The great mass of this sulphur is in the form of hydrogen sulphide, H_2S. The rest consists principally of carbon bisulphide, CS_2, with some other sulphur compounds practically negligible in quantity. This is an advantage from the standpoint of purification, as the H_2S is the easiest to eliminate. It can, in fact, be removed almost completely by the simple process of passing the producer gas through a filter containing oxide of iron, which reacts with the hydrogen sulphide, so as to form sulphide of iron.

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*From the Iron Age.

THE FILTERING MATERIALS.

Among the filtering materials most successfully used is ferox, a prepared oxide, the base of which is a natural iron ore, washed and crushed. By a process of concentration this is freed from mechanical impurities, then placed in retorts. In the retorts all of the water that is in combination with the ferric oxide is driven off, together with other chemical impurities, leaving only the oxide and a certain percentage of free silica to give porousness to the mass, which is further lightened, when placed in the filter, by the addition of wood shavings. The latter also serve to catch any particles of tar that may have escaped the scrubbing and washing process. The reaction in the filter may be assisted by a special "intensifying" chemical, added as a powder, the exact nature of which is not divulged.

In putting the oxide into a purifier, the trays are first covered with a light layer of shavings, then a foot of oxide mixed with shavings is spread over the surface, stamped down and tamped hard along the edges of each tray and around each pipe inlet and outlet. A bushel of wet shavings to each 30 lbs. of oxide, stirred together with a fork, is about the right mixture. Additional layers are placed in the same manner, according to the height of the tray.

Besides the material mentioned there are filtering substances known as iron sponge, hydroxide and lavino, which have proven very efficient. To remove the sulphur from each 100 ft. of gas in ten hours requires about 1.5 to 5 cu. ft. of oxide, depending upon the sulphur content.

FILTER BOX CONSTRUCTION.

There are several methods of constructing the filter boxes, particularly in providing for the entry and outlet of the gas. One is to admit the gas at the middle of one end, let it flow both up and down through the layers of oxide and out through a common orifice at the other end. This method is favored where a saving in space seems desirable. The better practice seems to be to have the gas pass one way only, and preferably down.

The gas should have a rate of flow through the filter bed of not more than 12 in. per min., and the depth of the oxide should be such that the gas will take at least 12 min. to pass through. To provide for this requires an aggregate depth of 12 ft. of oxide, arranged preferably in four layers of 4 ft. each, three in service and one cut out for regeneration or refilling. The temperature of the gas in the box should be 90 to 100° F., to get the best results, particularly when starting up a filter; but in regular continuous operation the necessary reaction will ordinarily take place at any temperature down to, say, 60° F.

REGENERATION.

The process of regenerating the oxide is a very simple one. It merely means taking out the trays and spreading the filtering material so as to expose it to the atmosphere. This causes a second reaction by means of which the sulphide of iron formed in the filter is converted back into oxide, the process being commonly known as "reviving" or "regenerating," and free sulphur is deposited. In this way the filtering material can be used over and over again until the percentage of sulphur becomes too high.

Reviving the oxide in the filter by means of an air blast is also practiced; or air may be drawn down through the mass. If, however, the filter boxes are rotated on the backward cycle system, the oxide can be fouled up to 60 or 70 per cent with only one regeneration in the open air. Reversing the direction of flow through the beds, also, has been found advantageous. In reviving by any system precaution against fire needs to be taken, as the oxide heats rapidly and spontaneous combustion is liable to result.

Until quite recently oxides consisting of rusted borings and turnings were used almost exclusively in this country; but, as a purifying material for coal gas, manufactured by illuminating companies, these were not satisfactory, and in the case of producer gas they proved ineffective. Hydrated iron ore, or "bog iron," utilized to some extent, is apt to become inert after the first fouling. The introduction of especially prepared anhydrous iron oxides has worked a revolution in the purification of illuminating gas; and absorption tests on producer gas show that the sulphur can be as easily removed as in gas-works practice.

Analyses of coals from different sections of the country, used for producer tests, show that a heavy sulphur content is quite likely to be accompanied by a high percentage of volatile matter and other characteristics which would mean a good gas yield. Under the conditions heretofore prevailing, such coals are shut out from consideration as fuel for producers serving open hearth furnaces; but, with iron oxide purification, there is no reason why many such cannot be used. An objection found to purifying producer gas for furnaces is the fact that it must be passed through the filter at temperatures considerably under normal, involving a loss of thermal units from cooling; but the advantages far outweigh any operating loss from this cause.

A report entitled "The Pottery Industry" has been issued by the Department of Commerce through the Bureau of Foreign and Domestic Commerce. It is the result of an investigation of the cost of production, profits of manufacturers, wages and working hours, and other conditions in the pottery industry in the United States, England, Germany, and Austria.

THE STATISTICAL POSITION OF SPELTER.*

The unprecedented and spectacular rise in the price of spelter in January and February of 1915 has caused the statistical position of spelter to be examined as never before. The large stocks at smelters at the beginning of 1914, the much larger stocks at smelters at the mid year, and the great demands for zinc for export for war purposes have served to augment the deep interest in this metal. Spelter at St. Louis went from $0.047 on August 8, 1914, to $0.107 at the end of February. The estimated total annual consumption of spelter in the United States is 378,500 tons.

If spelter-consuming industries in the United States enjoy prosperous conditions in 1915, so that the total spelter consumption makes its normal gain (which, however, in view of the high price of spelter and the resulting effect on domestic consumption is scarcely probable). figured on the totals for the last six years, the total domestic spelter consumption for 1915 would approximate 397,000 tons. If to this we add a year's domestic exports at the rate shown since the beginning of the war in Europe—180,000 tons—and a year's foreign exports (reexports) at the rate during the latter half of 1914, equal to 17,000 tons, we get 594,000 tons as the possible demand for spelter. This, however, is not the maximum possible quantity to be demanded. Attention was directed by the United States Geological Survey in a press bulletin, in August, 1914, to the opportunity for the American zinc industry to supply the major part of 222,000 tons of export spelter a year as long as the war lasts. Exports of spelter for seven months have been made at the rate of 197,000 tons yearly. Moreover, there remains the possibility of the trade in galvanized sheets, wire, and products with the southern continents and Asia. So far this has not been touched. The exports of galvanized sheets in 1914 were 45,318 short tons, compared with 86,475 tons in 1913. The exports of barbed wire, plain and galvanized, were 105.078 tons, as compared with 107,586 tons in 1912. When the United States comes into its share of the trade in galvanized products with the southern continents and Asia the domestic consumption of spelter will be increased and will in turn increase the total possible demand for zinc given as 594,000 tons above.

On consideration, the domestic smelting capacity seems scarcely more than equal to this possible demand. The total number of ordinary retorts completed and contemplated at the close of 1914 is 124,016. Some of those contemplated can not be completed before the latter part of the present year. If we estimate the average capacity per retort as 4¼ tons of spelter per year, the capacity of 124,016 ordinary retorts, together with the large retorts listed, is approximately 535,000 tons. Add to this 20,000 tons of stocks on hand and 30,000 tons of remelted spelter, we get 585,000 tons. If we take into account that the maximum smelter capacity indicated above can not be reached until the latter part of the year, and consider the possibility of increased demand for galvanized products, it seems very improbable that there will be any surplus smelter capacity or accumulation of spelter stocks during the year. Apparently a continued decline in prices can come about only by a slackening in the foreign demand for spelter for war purposes.

It remains to consider whether the zinc resources of the United States, together with the contiguous countries usually drawn upon, will be equal to the possible demands of the immediate future.

Table I shows the leading position of the United States in the world's production of spelter (in tons of 2,000 pounds):

TABLE I.

Locality in which smelted—	1906.	1907.	1908.	1909.	1910.	1911.	1912.	1913.
Australia	1,131	1,098	1,198	....	560	1,904	2,531	4,105
Austria and Italy	11,883	12,522	14,063	13,931	14,666	18,602	21,609	23,928
Belgium	168,067	170,307	181,851	184,194	190,233	215,050	220,678	217,928
France and Spain	59,293	61,438	61,512	61,859	65,191	70,791	79,543	78,289
Germany	225,997	230,058	239,062	242,594	251,046	276,008	298,794	312,075
Great Britain	57,971	61,286	60,029	65,422	69,531	73,803	63,086	65,197
Holland	16,150	16,526	19,017	21,548	23,121	25,059	26,380	26,811
Norway	....	....	....	....	....	7,363	8,959	10,237
Poland	10,595	10,735	9,740	8,758	9,514	10,952	9,659	8,389
United States	224,770	249,860	210,424	255,760	269,184	286,526	338,806	346,676
Total	775,857	813,830	796,896	854,066	893,046	986,061	1,070,045	1,093,635
United States percentage of world's production	29.0	30.7	26.4	29.9	30.1	29.1	31.7	31.7

U. S. Commercial Attaché V. L. Havens, Santiago, under date of January 8, states that he has been advised that the production of iodine in Chile could be doubled at exceedingly small expense, but that an organization controls the world's markets through contracts, and if the production of iodine should be increased by any nitrate producer it would be at his own risk and loss. Some of the nitrate companies which produced too much last year are not allowed to sell any this year. If some new use could be found for iodine by an industry not associated with the organization it should be able to obtain a large and cheap supply from Chile.

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*From a bulletin of the U. S. Geological Survey.

RITTMAN GASOLINE AND BENZOL PROCESSES.

In view of the large public interest being taken in the gasoline and benzol processes devised by Dr. Walter F. Rittman, chemical engineer of the Bureau of Mines, Secretary of the Interior Lane, has issued the following statement:

Excellent progress is being made in the development of the Rittman processes and there is every reason to believe that both the gasoline and the benzol processes will be on a commercial working place within a reasonably short time. I am informed that the gasoline process is now ready for large scale industrial application and the hope is expressed that the benzol process will be ready soon.

The benzol process is being developed in co-operation with the Aetna Chemical Co. of New York, which company has entered into an agreement whereby all patentable equipment, processes and ideas available as a result of the co-operative work will be turned over to the department to be dedicated to the public.

The department stands ready and is anxious to enter into similar agreements with any other companies in the country that will agree to the same terms —that all processes and ideas patentable in the development of either process shall be turned over to the department for the use of the public. The department is willing for all who are desirous of making use of the processes to do so to the fullest possible extent consistent with the proper protection of the processes in order that the public may derive the greatest measure of benefit therefrom. It looks as if it would be only a short time before the complete mechanical equipment necessary for the practice of the processes has been worked out and the inventions covered by patent applications.

The department consider that all those desirous of employing the processes should agree to contribute to the public in the same manner that Dr. Rittman has done with his basic patents, all patentable ideas that may be conceived as a result of the employment of these processes. This is the only condition that the department imposes and its reasonableness will become apparent when it is considered that Dr. Rittman has given to the public, through the department, processes which conservatively might be worth millions of dollars were they controlled by a private industrial concern, exclusively for its selfish purposes.

As soon as the department is assured that the public's interests are properly safeguarded a full and complete scientific paper describing the processes will be issued. In the meantime the processes will be open to any one who wishes to develop them under the conditions imposed.

At the first public demonstration of the Rittman benzol and gasoline processes held March 8, before the representatives of the Army and the Navy, the General Chemical Co., the Aetna Chemical Co., the Standard Oil Co., of Indiana, the du Pont de Nemours Powder Co., and some twenty or more represenstatives of the National Petroleum Association and other prominent refining interests throughout the eastern part of the United States, announcement was made that both processes might be used by all interested persons upon application to the department. At the same time, however, because of the desire to give the public the fullest possible benefits of the Rittman processes, it was stated that the use of the processes would be coupled with the condition that the persons using the same would give to the public the benefits of such ideas along mechanical lines as they might conceive during the employment of the processes.

A number of Wetsern and Mid-Continent refiners, who were unable to be present at the first demonstration, recently requested the department to give them an opportunity to witness the workings of the processes, and for their benefit a demonstration was held on May 14, which was attended by accredited representatives of the Waverly Oil Co., Western Petroleum Refiners' Association, the Vacuum Oil Co., the Atlantic Refining Company, the Butler County Refining Company and others. As a result of this latter demonstration, it is expected that several of the refiners will employ the Rittman processes in their works under conditions similar to those which have already been agreed to by the Aetna Chemical Co.

IMPORTS OF TOMATO PASTE.

American canners are taking an interest in the rapidly growing imports of tomato paste, or sauce, from Italy, and it is not unlikely that efforts will soon be made to keep at least a part of this business at home. The total imports of the paste in 1913, according to Commerce Reports, were valued at $2,801,974 and weighed approximately 13,000 tons.

The tomato product imported into this country from Italy is made by crushing the tomatoes, straining out the skins and seeds, and reducing the pulp to about one-fourth its original volume by evaporation in vacuum boilers, although for special purposes it is reduced to as little as one-twelfth. It is used in Italy in a great many dishes, perhaps the most familiar of which to Americans is spaghetti. The demand for the sauce in this country originated among Italians living here, but a knowledge of its excellence has been gained by others and its use is increasing. There seems to be no good reason why American canners can not meet this demand, especially as the Italian factories have demonstrated what machinery is best suited for the purpose. Very little experimenting will be necessary here, so far as machinery is concerned.

So far the imports have been confined almost entirely to the sauce, but it is not unlikely that continued success in that line will lead to the introduction of Italian canned tomatoes, which have already become very popular in England.

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NOTES AND COMMENTS.

Unprecedented Demand for High-Speed Steel.

U. S. Consul John M. Savage, Sheffield, England, in a report under date of April 16, states that the most striking feature of Sheffield's trade today is the remarkable boom in high-speed steel. In the history of the trade nothing approaching the present demand for this article has heretofore been experienced; in fact, the present colossal requirements have never been dreamed of. Not only are orders numerous, but they are of tremendous size and value. These orders, in addition to British sources, come from Russia, France, Italy, and the United States. One order received this week from Russia amounted to 100 tons. This does not seem a large quantity when speaking of steel to those unfamiliar with the trade, but the importance of the order can be gauged by the fact that this material is quoted by the pound, and the price today is from 41 cents to 97 cents, as against 32 cents to 85 cents in normal times.

An immense quantity of this steel is necessary in the production of armaments, and every engineering shop in England is busy on this work.

The resources of this city for meeting the increased demand are totally inadequate, many firms having been compelled to refuse orders because of their inability to take on additional business.

In the manufacture of high-speed steel the principal alloys used are tungsten powder or ferrotungsten, ferrochrome, and ferrovanadium, and the supply of these alloys has failed to a great extent, which has been a further handicap to manufacturers.

Prior to the war it is estimated that Germany supplied 90 percent of the tungsten used by British manufacturers, and since then this source of supply has been entirely cut off. British firms are endeavoring to supply this deficiency and expect to be able to place their products on the market by midsummer, although there is no certainty as to this. In any case it is thought the present high prices prevailing will continue throughout the year.

Ferrochrome (4 to 6 carbon) has advanced from 30 to 35 percent.

The price of vanadium has remained stationary, owing to the fact that almost the entire supply comes from the United States, where there is ample production.

Ferrotungsten has advanced from 57 cents to 97 cents per pound of tungsten contained in the alloy.

Tungsten powder (from 96 to 98 percent pure) has made the phenomenal advance from 57 cents to $1.34 per pound.

In former times tungsten powder was the favorite form of wolfram used by local manufacturers. Since then, however, owing probably to the difficulty experienced in procuring wolfram in this form, ferrotungsten is being extensively used.

Hearing on Flour Transferred to Washington.

The hearing to discuss definitions and standards for various kinds of flour called for May 24 in St. Paul, Minn., has been postponed and transferred to Washington. This hearing, which is to be held by the Joint Committee on Definitions and Standards, composed of representatives of the Association of American Dairy, Food and Drug Officials, the Association of Official Agricultural Chemists, and the United States Department of Agriculture, will be held in the Bieber Building, No. 1358 B street, S. W., Washington, D. C., Saturday, June 5, at 10 a. m., before the entire committee, which is to be in session in Washington from June 1 to that date.

Swedish Iron Industry.

The Swedish Iron Workers Union met November 28 and made a report on the industrial situation. According to their report iron manufacturing and export have considerably diminished this year owing to the war and the lack of water for power, etc.

The war has almost paralyzed the iron business both to belligerent and to neutral countries, and even the new markets opened by the war situation have not succeeded in greatly ameliorating the outlook.

Exportation was at its lowest during August, when it sank to 13,600 tons, as against 47,800 tons in August, 1913. During September and October there was a slight turn for the better, exports being, respectively, 32,400 tons and 33,200 tons, as against, however, 45,400 tons and 55,500 tons in 1913.

Iron ore has also dropped so hard that statistics show a diminution in export of 1,472,000 tons this year in comparison with the export of 1913.

Owing to the lack of water, the works in Sweden can not manufacture enough even to meet the demands of the reduced Swedish consumption of iron and steel. Thus prices have kept steady and even rising, which helps to make amends for the increased manufacturing expenses, higher coals, increased export rates, increased war insurance, etc.

Unfortunately, also, the question of the new water rights for power has not yet been settled, so that no ordering of water current can as yet be arranged.

On October 31, 66 blast furnaces were at work, as against 108 in 1913, constituting, respectively, 53 percent and 87 percent of the whole number; 110 "Lancashire" forges were operating, as against 210 the preceding year, or, respectively, 42 percent and 81 percent of the whole number; 9 Bessemers, as against 17 in 1913, or, respectively, 37 percent and 71 percent of the whole; 49 open hearths, as against 62 the previous year, or, respectively, 65 percent and 87 percent of the whole number.

Cast-iron production during July to September amounted to 140,300 tons, as against 175,800 tons for a like period the preceding year. Blooms in the quarter in 1914 totaled 23,800 tons, in 1913 38,600 tons; Bessemer ingots, 21,100 tons in 1914 and 27,700 tons in 1913; open-hearth ingots, 90,900 tons in 1914 and 119,900 tons in 1913.

Radium and Vanadium Production.

The year 1914 was eventful in the industry of mining radium, uranium, and vanadium ores and had by far the largest year's production in the United States. Figures collected by the Geological Survey indicate that the output amounted to about 4,300 short tons of dry ore carrying 87 tons of uranium oxide and 22.4 grams of metallic radium. The ore was valued at about $445,000. The ore produced in 1913 contained 41 tons of uranium oxide and 10.5 grams of radium, and that produced in 1912 contained 26 tons of uranium oxide and 6.7 grams of radium. About nine-tenths of the contained radium is thought to be recoverable under improved processes.

Early in 1914, owing to the very high prices charged for radium salts, their scarcity, their evident usefulness in treating cancer and other hitherto incurable diseases, the practical impossibility of the poor receiving treatment by radium because of its scarcity and high cost, and to the fact that much of the radium-bearing ore was being shipped out of the country, Secretary of the Interior Lane caused to be introduced in Congress bills reserving radium-bearing lands from entry as mining claims, and providing for government purchase. The bills are still pending.

During the year the National Radium Institute conducted, under the supervision of the Bureau of Mines, mining operations in Montrose County, Colo., and a plant at Denver for producing radium and investigation of processes. The work has been so encouraging that Director Holmes has announced the probable production of radium at one-third of its present cost.

In Utah the Standard Chemical Co. made the first commercial production of carnotite ores and the commercial production of uvanite, a radium-bearing mineral new to science, accompanied by other uranium minerals, was begun. This company and the Radium Co. of America produced radium salts during the year, and Dr. W. A. Schlesinger started a radium-refining laboratory. The European war stopped nearly all operations in both mines and reduction plants, for the two companies sold their product largely in Europe and practically all the ore bought by brokers was sold abroad. A little more than 1,200 tons of ore, containing 28.1 tons of uranium oxide and 7.2 grams of radium, was consigned to Europe, but as the foreign refineries were closed, a part of it was held in transit.

No vanadinite or similar ores are known to have been sold for vanadium during the year, but a number of mines in New Mexico and Arizona shipped and sold such ores for their lead and silver contents.

Cuban Sugar Output.

The following table from *Cuba Review*, March, 1915, shows the output, in bags of 325 pounds net, of the active sugar plantations of Cuba during 1914 and the estimates for 1915, by Provinces:

Provinces.	1914. Bags.	1915. Bags.
Habana	2,117,026	2,077,000
Pinar del Rio	352,002	317,000
Matanzas	3,634,294	3,853,000
Santa Clara	5,175,559	5,360,000
Camaguey	2,062,998	1,995,000
Oriente	4,515,939	4,414,000
Total	17,857,818	18,016,000

According to the *Review of River Plate* of April 16, nitrate exports to the United States can now be considered to be normal; direct exports of nitrate to Italy, Denmark, and Sweden have increased; to Spain exports have increased slightly; to France they have diminished to one-third of the normal; and to Germany and Belgium they are entirely suspended.

POSITION WANTED as assistant chemist. Completed the I. C. S. General Chemistry Course and the manufacture of sulphur and hydrochloric acid. Married. Have a responsible position in another line of work; desire a change. Box 6, Chemical Engineer, Chicago, Ill.

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DISINFECTANTS AND DISINFECTION.

By JAS. J. BOYLE.

Written for The Chemical Engineer.

Owing to the marked attention sanitation has recently received, based chiefly on the germ theory of disease, a large manufacturing company requested the writer to investigate the subject of disinfection with the object of purchasing efficient and economical disinfectants.

The investigation proved interetsing, and, believing the information obtained had an educational value, it was decided to publish it, omitting such data as was considered unnecessary.

A survey showed the market is literally flooded with proprietary disinfectants of varying degrees of effectiveness. Many are frauds, several of very limited value, while others, though possessing merit, are often exorbitant in price.

Knowing how eager the public is for things pertaining to sanitation, several of these disinfecting companies have exploited their questionable products to the utmost.

A careful study of the problem shows it is plainly evident something should be done to protect this unsuspecting public against the wiles and rapacious greed of these unscrupulous concerns.

Only one state, Marylanad, has laws regulating the sale of disinfectants. There the manufacturers are required to state the phenol coefficient on the label of their products. It is understood New York is about to enact similar legislation.

The chief object of the investigation was to examine some of the best known and most representative disinfectants found on the market, and compare them on a unit price per coefficient basis as advised by the United States Hygienic Laboratory in Bulletin No. 82.

In the combined interest of economy and efficiency, disinfectants then should be bought on the basis of their germ killing power, which is determined by comparing the power to kill typhoid (the standard germ), with that of pure phenol (the standard germicide). The ratio obtained in germ killing power is expressed as a number and is called the phenol, or carbolic acid, coefficient.

Of the various methods for determining this coefficient, the Rideal Walker is the one most generally used, and will likely become the standard. The method of the U. S. Hygienic Laboratory is considered very good and is frequently employed.

Much confusion on the coefficient question now existing would be eliminated if a standard method were adopted. As a rule, the Rideal-Walker method gives higher results than that of the U. S. Hygienic Laboratory.

A disinfectant having a coefficient of 2 or 10 means that it is 2 or 10 times as efficient as pure phenol in killing typhoid germs.

The standard dilution of pure phenol for general disinfection is 1 in 25, making a 4 per cent solution. The proper dilution then for any disinfectant for general use is obtained by multiplying the coefficient by 25. In order to compare costs, and to prepare the proper dilution, it is necessary to know the phenol coefficients of disinfectants.

The comparison Table I was made by dividing the cost per gallon by the coefficient of each of the disinfectants which gives the unit price per coefficient. The

TABLE I.—SHOWING COMPARATIVE COST OF DISINFECTANTS ON A PHENOL COEFFICIENT BASIS.

Firm.	Disinfectant.	Coefficient.	Price per Gallon.	Unit price per Coefficient.	Price per Gallon Diluted Ready for Use (1 in 25).
I.	A-1	2	$0.40	$0.20	$0.008
	A-2	4	.50	.12½	.005
	A-3	5	.60	.12	.0048
	A-4	6	.65	.108	.0043
	A-5	8	.80	.08	.004
	A-6	20	1.50	.075	.003
II.	B	4½	.55	.122	.0049
III.	C-1	19	.83	.0437	.00175
	C-2	3	.90	.30	.012
IV.	D-1	2½	1.00	.40	.016
	D-2	2½	1.00	.40	.016
V.	E-1	6	1.00	.166	.0066
	E-2	20	1.50	.075	.003
VI.	F-1	2	.60	.30	.012
	F-2	4	.65	.16	.0065
VII.	G-1	15	1.25	.083	.0033
	G-2	6	.65	.108	.0043
VIII.	H-1	20	1.10	.005	.0022
	H-2	15	1.25	.083	.0033
	H-3	9	.85	.094	.0033
	H-4	1.35	1.25	.926	.037
IX.	I-1	7	.60	.086	.0034
	I-2	20	1.10	.055	.0022
X.	J	Not given	1.25	....	.....
XI.	K	Not given	1.25	....	.....

price per gallon ready for use (1 in 25) equal to a 4 per cent phenol solution, was found by multiplying the coefficient by 25 and dividing the product obtained into the price per gallon. For obvious reasons, the names of the various companies and their products have been omitted.

All the disinfectants listed in this table were coal tar products except H-4 and K, which were formaldehyde preparations, and J, a potassium permanganate solution.

An examination of the table shows C-1, H-1, and I-2 are the cheapest disinfectants on a unit price per coefficient basis. The unit price per coefficient generaldecreases as the coefficient value increases, hence the high coefficient products, ranging from 18 to 20, make the most economical purchase.

Of the two formaldehyde disinfectants listed, only one had a stated phenol coefficient value, and that so low it did not compare favorably with the coal tar products. Analysis showed it to be essentially a mixture of zinc chloride and formaldehyde. K, the other formaldehyde disinfectant, was analyzed and found to be a very weak solution of formalin. It could be made for about 6c per gallon. Formaldehyde is a valuable agent when used in the form of a gas, but becomes efficient in that form only if the room in which disinfection takes place is closely and positively sealed and made air tight. It is impractical for use in the 5 per cent solution usually recommended for proper germicidal efficiency on acount of its bad irritating effect on the mucous membranes of the nose and respiratory organs.

J was analyzed and found to be a very weak solution of potassium permanganate. The price asked per gallon for this material was $1.25, but it could be duplicated for less than 1c a gallon. It will be noted a fine profit is made on this product.

Concerning potassium permanganate, Roseneau, in *Disinfection*, says: "Potassium permanganate is a germicide of undoubted power, but of very limited application in general practice on account of the readiness with which it is reduced and rendered inert by organic matter. Even in weak solutions, it destroys micro-organisms of high resistance, and despite its limitations, it ranks high on the list of disinfectants for certain definite purposes. Its nascent oxygen is the true disinfecting agent. Harrington says for general disinfection a large amount of salt is necessary for a small amount of organic matter. Thus, one ounce of liquid feces or urine can reduce such an amount that it is estimated that the sterilization of the total twenty-four hours excreta of one person would cost five dollars."

An examination of the coal tar products showed great latitude in refinement; several had a strong coal tarry odor, rendering them unsatisfactory for indoor disinfection, while others were well refined and possessed an odor approaching phenol. These products were also examined for solubility in water, for heavy oils, corrosiveness, and effectiveness as a cleanser on wood, varnish, metals, etc.

Frequent standardization of these products is necessary on account of wide variance in composition. Several of the companies, particularly the smaller ones, have their products tested once or twice a year, believing that is all that is necessary to insure the uniformity of their product.

One of the largest and most reliable disinfecting companies, who very frequently standardize their products, had the contract to supply a large city with a guaranteed disinfectant of high coefficient. A casual examination by the city once showed the coefficient value to be below the stipulated figure, and, needless to say, much unpleasantness followed before the matter was satisfactorily settled. This case is cited to show the need of frequent standardization.

In regard to the use of drip disinfecting machines for toilet disinfection, the writer has always been vigorously opposed to them, and has combatted their installation. Lately, the tendency among the large disinfecting companies has been to abandon these, and rely more on deodorizing machines.

Replying to an inquiry on the question of the drip disinfecting machine for toilet disinfection, one of the best authorities in this country writes as follows: "I do not advise the installation of the so-called drip disinfection machine for toilet disinfection, as it is my firm opinion that these machines are practically of no value in the disinfection of discharges deposited in the toilet."

Owing to poor janitorship, inferior plumbing or poorly situated toilets, it is necessary at times to suppress bad odors by the use of deodorants, or to be more exact—reodorants. These products, which act in various ways, simply replace one odor with a more pleasant one, and are usually without any sanitary significance. Their use should be limited, for they often mask an unsanitary condition that otherwise would be quickly detected.

As a routine practice, cleanliness in this respect is above all other modes of procedure in sanitation, and in private houses is all that is required.

In purchasing coal tar disinfectants, the label often states the product to be non-toxic. This is a misleading statement, for all these products are more or less toxic and when using them this should constantly be borne in mind.

The U. S. Hygienic Laboratory in Bulletin No. 88 gives a number of these mis-labeled coal tar disinfectants, with a report on their relative toxicity. This bulletin should be in the possession of every one desiring information on the subject.

CONCLUSIONS.

The coal tar products are the best general disinfectants.

They should be purchased on phenol coefficient basis.

They should be standardized frequently, have good cleansing properties, and form practically perfect emulsions with water.

It should be distinctly remembered they are all more or less toxic.

Drip disinfecting machines are inefficient and should be abandoned.

There is urgent need of legislation to cover the disinfectant question.

BRITISH SOLUTION OF THE DYESTUFF PROBLEM.*

It was quickly recognized after the outbreak of the present war that by far the gravest economic problem for British industry resultant from the European conflict was associated with the complete cessation of dyestuff imports from Germany.

Great textile and other industries were absolutely dependent upon a regular supply of coal-tar dyes. The value of the annual output of these industries exceeds $1,000,000,000. The workmen employed number over 1,500,000. The annual consumption of artificial dyes in these industries exceeds in value $10,000,000. British manufacturers supply 8 per cent of this amount, but depend to some extent upon Germany for half-manufactured material. Germany has supplied 80 per cent of the finished dyes. The remaining 12 per cent have come chiefly from Switzerland, and this source has been curtailed, largely on account of the dependence of Swiss manufacturers upon German intermediates.

Practically the great textile interests of Great Britain are dependent upon German color works for their continued existence under hitherto existing conditions.

The dangers and the humiliation of such complete dependence have been acutely felt by British industrialists, economists, and statesmen, and have been the subject of profound study and widespread discussion for months. Various methods have been proposed for solving the problem, which has become more threatening with each day's delay. Methods that would be readily feasible in France, with its avowed protectionist principles, seemed totally inapplicable when brought face to face with the stern determination not to break with the traditional free-trade policy of the Kingdom.

As a result of these months of discussion a few cardinal principles have been evolved and a concrete plan for meeting the issues has been formulated and set in active operation.

The conclusion to which the British Government and British industrials have come are as follows:

The United Kingdom must have its own independent, self-contained, coal-tar chemical industry, using British raw materials.

The industry must be big enough to take advantage of the economies of manufacturing on a large scale.

It must be distinctly a national industry, under no temptation to succumb to offers of purchase or absorption by international rivals.

It must be co-operative, based upon a joint interest between producer and consumer.

The form in which these principles are to find active expression was decided upon early in March, when the national company, incorporated as the "British Dyes (Ltd.)," was organized at Manchester, the center of the English textile industry.

Its capital was placed at £2,000,000 ($9,733,000). The British Government loans, in addition, £1,500,000 ($7,300,000) at 4 per cent to be repaid in 25 years. Dividends are limited to 6 per cent until the Government loan is repaid. The Government grants $500,000 for a research laboratory. The Government is also represented by two members on the board of directors, which is composed of nine members in all. These Government delegates have a controlling vote on many questions, as is evidenced from the following regulation:

The Government directors, jointly, or if only one be present, then that director, shall, in addition to their ordinary votes as directors, have absolute power to veto any proposal or resolution of the board which, having due regard to the main object with which the company has been formed, shall in their or his opinion tend to encroach unduly on the trade or business of any British manufacturer of products other than dyes or colors; or to give any undue preference as regards supply, prices, or otherwise to any customer or consumer of the company's products. Provided always that such veto shall not be used in such a manner as to prevent the manufacture or rendering marketable of products incidental to the manufacture of dyes or colors or to prevent priority of supply for shareholders.

Shareholders will have priority in receiving the available supplies of the company. It is expected that the stock will be taken almost entirely by dyers and others who are users of dyestuffs, and it is hoped to have all British consumers of coal-tar chemical products included among the shareholders.

An option was secured at an early date upon the largest existing plant in England for the manufacture of aniline dyes, that of Read, Holliday & Sons, at Huddersfield. The right of option was exercised on April 23. On May 3 the transfer of the plant to British Dyes (Ltd.) took place, and actual manufacture under the new management began.

The firm in question was established in 1830, and was one of the first to embark extensively in the manufacture of coal-tar colors. The works cover an area of 150 acres and give employment to 750 operatives. An American selling agency has been maintained at New York with branches in five other cities. Provision is made for the two leading managers of the firm to be retained in the management of the new company.

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*From Commerce Reports of U. S. Department of Commerce.

Other color works are to be acquired, and the whole industry is to be consolidated, co-ordinated, and greatly enlarged. Some time will necessarily elapse before the new undertaking can satisfy the British demand, but there appears to be a resolute determination to create a national industry upon a permanent basis.

The final success will evidently rest, not only upon the generous co-operation and aid of the Government, but also upon the identification of the great mass of British consumers of dyestuffs with this new movement as holders of its shares and ultimate controllers of its policy.

The organizers have decided to issue at first stock to the extent of £1,000,000 ($4,866,000), one-half of the prospective capital. Subscriptions came in with some slowness and evident hesitation. In several cases large subscriptions were accompanied by conditions. The causes for these conditions were removed by various modifications in the original plan. Early in April the unconditional subscriptions reached a total of £636,000, or nearly two-thirds of the required amount.

By this time it was evident to the organizing board that the bulk of the needed capital was in sight, as several corporate bodies who are prospective subscribers are delayed in making applications until statutory meetings can be held. It was accordingly decided to allot stock at once to all subscribers and proceed with the program of manufacture. A quarter of the par value of stock will be paid at once. Six months must elapse before another call for partial payment can be issued. The British Government advances at once an amount equal to that subscribed. Note should be made also of a further sum of £200,000 ($973,000) loaned by the Government in 1914 to Read, Halliday & Sons for the purpose of urgent extensions.

This capital is regarded as ample to meet the necessary demands for establishing the future industry on a generous basis capable of natural but rapid evolution, and destined to ultimately supply the major portion of the artificial dyestuffs required by the nation's industries.

The whole movement has evoked from its inception a vast amount of discussion, largely on account of the exceptional attitude of the British Government in granting such liberal aid to create a national industry.

As the question of emancipating the vast textile interests of the United States, and numerous allied industries, from dependence upon foreign dyestuffs is now a matter of such active agitation, a brief résumé of the attitude of various British industrial and economic authorities to the plan outlined above may be instructive and suggestive.

The scheme at the outset included a pledge by all stockholders to use exclusively dyes made or provided by the new company during a term of five years after the conclusion of the present war.

This awakened much adverse criticism and antagonism, and was finally withdrawn. The withdrawal had much to do with obtaining the later subscriptions necessary to insure financial success.

As the prospectus assured priority in furnishing dyestuffs to shareholders, a certain amount of criticism was awakened regarding the position of the many small dyers, unable to subscribe to any extent, and yet large users of coloring materials. The assurance was finally given that the attitude of the new company toward this class would be sympathetic, and that no undue discrimination would be made in allotting dyestuffs, careful consideration being given to the financial ability of the class in question.

A general order in regard to the utilization of foreign patents was issued by the British Government some months ago by virtue of which British manufacturers are granted permits to use processes protected by patents that are the property of persons or firms resident in belligerent countries. Reasonable royalties are to be paid the owners, and the right of manufacture, after the war, without interpretation or hindrance, on the same basis, is fully guaranteed.

This privilege is a most useful asset for the new company. It enables it to start at once the manufacture of nearly all the important dyes brought upon the market since the opening of the century, notably the valuable indanthrene colors, with the certainty of being able to continue the manufacture after the close of hostilities on the payment of equitable royalties.

Equally important are the provisions made by the British Government for the liberation from the payment of internal-revenue tax of all alcohol required in the coal-tar color industry.

There has been a vast amount of discussion connected with relations to the Swiss dyestuff industry. The group of large color works at Basil form an important factor in the international dyestuff question. The annual output is valued at $6,100,000, including synthetic indigo, worth $750,000. In regard to finished dyes, the Swiss industry is almost as well rounded as the German industry. Its weak points are the dependence to a great extent upon Germany for intermediates or semi-manufactured material and the absence of a domestic source of coal tar and of benzol.

Soon after the outbreak of war the Swiss factories were seriously crippled. Customary supplies from Germany were cut off unless guarantees were given that no dyes would be supplied to France, Great Britain, or Russia. Such guarantees were refused. Arrangements were then made to send coal-tar crudes and some intermediates from Great Britain to Switzerland in return for finished dyes. Provision was made to facilitate the transport both ways across France.

This trade is to be transferred to the new company.

which will care for the shipment of the raw material and for the merchandizing of the finished products.

Not a few have urged the adoption of a policy based essentially upon the utilization of the well-equipped Swiss industry, with its fine plant and large staff of experienced chemists.

British purchases of artificial dyes from Germany average annually somewhat over $6,100,000, including about $370,000 worth of synthetic indigo. It was felt by many that the British demand might be switched permanently from Germany and that Great Britain might in turn release Switzerland from her dependence upon Germany for crude and intermediate coal-tar products. This plan was rejected, as Great Britain would still be economically dependent upon a foreign country for its color supply.

An alternative plan contemplated the acquisition by the new British company of the more important Swiss firms, or at least their control, by the purchase of a majority of the shares. The total capital of the Swiss color companies is about $3,500,000, and the employees number 3,500. This would involve close co-operation and a practical transfer to British territory of Swiss methods, patents, and technical experience, along with a staff of Swiss chemists to shape in a large measure the expansion of existing British color plants to the dimensions of a national, self-contained industry. Simultaneously the British works would supply all primary coal-tar products needed normally by the Swiss factories. There is much involved in this proposition which may eventually prove attractive to the new British company, provided it is equally attractive to the Swiss interests. It would certainly save the managers of the British project a vast amount of expense and of effort in working out the details of the big problem before them.

It is very possible that an analogous plan for utilizing the accumulated capital of experience in the Swiss dyestuff industry and the close familiarity with every phase of the complex maze of interlocked and interdependent branches of manufacture might be the simplest method of solving the American problem.

The question has been raised whether it is possible to secure in the early future enough chemists in Great Britain to meet the needs of a vastly enlarged dyestuff production. Complaint has been made that no chemists are on the board of directors of the new company.

In this connection the President of the Board of Trade states that two leading British chemists recognized throughout Europe as authorities in the chemistry of dyetsuffs have been engaged. One of these received regularly, before the war, heavy retainers from one of the German dyestuff combines. He is confident that the best British chemical talent is equal to the best in any European country. A distinct difficulty he sees, at the outset, in finding enough second-grade chemists. This difficulty will gradually be overcome if adequate salaries are paid and a career is assured. At the same time he states:

> Another objection was that there was no scientist or practical professional scientific man on the board. While it might be desirable to have on the board of such a concern a chemist of great practical capacity, they also knew that firms of which the boards had been controlled by chemists had been brought to ruin. This matter had been anxiously weighed, and there were many business men who were quite convinced that it would be a mistake to have on the board of such a concern a man of special technical knowledge, because the whole of the other directors would be in his hands. The chemical director would say that he was the only man on the board who had any chemical knowledge and he must settle the matter.

Sir William Ramsay, who is at the forefront of British chemists to-day, combats this idea. He claims that the new undertaking is foredoomed to failure unless scientific chemists form an important part of the directorate, and cites a score of instances in the evolution of British chemical industry, as well as the brilliant German chemists, such as Caro, Martius, Brunk, and Bernthsen, all directors of the famous "Badische"; Duisberg, the leading spirit of "Bayers"; etc. In short, he concludes, it would be difficult to discover a successful chemical industry that has not been initiated and controlled by a chemist. Unless British Dyes (Ltd.) copies this precedent there is little hope for it.

The veteran chemist, Sir Henry Roscoe, himself a director of the Castner-Kellner Co., claims:

> In the color industry it is the research chemist, and he alone can keep the flag flying, for he alone can bring forward new forces and create new developments. Capital can not do it, business capacity can not do it; but the brains, the imagination, the skill, and the knowledge of the research chemist can. We have got the money, and we have got the men, but these must be put into their right places to do their work efficiently. To the general public the skill of the color chemist is a sealed book. His knowledge of the complicated constitution of his colors is both accurate and profound. He can manipulate them at will and can see the positions of their constitutents, in his mind's eye, as clearly as the patterns in a kleidoscope. Moreover, he can change these positions as he wishes. He can add to or subtract from these constituents and can thus produce a new compound possessing new properties. This is what is meant by research in the color industry. He may fail five times out of six to produce a new and valuable color, but the sixth is a success and brings with it financial prosperity.

From the very outset it has been recognized that the chief difficulty lies in the certainty that after the restoration of normal business relations between European countries the German color industry will hesitate at no measures to regain its past supremacy in the world's trade in artificial dyestuffs. A protective tariff is claimed by some as offering adequate means of defense and as warranted under the circumstances. The majority feel that it would not suffice; that more radical weapons are absolutely essential.

Sir William Ramsay declares in this connection:

No "protection" from foreign competition will save the situation. The only measure is the total exclusion of German dyes. Even yet we are blind to methods of German commerce. German manufacturers, backed by the whole power of the German State, will undersell our producers of dyestuffs, secure the whole market, and thus establish a monopoly. That has been their policy in the past; it will be their policy in the future. Let us be warned in time. There is ample chemical talent in this country, both scientific and technical. Every chemist is anxious to serve his country. What is needed is to call together a council of chemists, ask for their collaboration in investigation, and for their advice. Also, it should be announced that it is intended to exclude absolutely the importation of all German dyes, and capital will flow in.

Any other policy is shortsighted. The German chemical industry is worked as a huge trust, backed by the whole power of the German State. The French and the Russians are seriously considering this policy of exclusion; and if Britain still permits imports this will be the dumping ground of all Germany's chemical products until, competition being strangled, we shall have to pay exorbitantly for all manufactured articles imported.

The *Chemical Trade Journal*, an outspoken critic of the undertaking, outlines the following policy as essential:

The fundamental basis of any scheme that is intended to achieve success must be the elimination of German competition, either by means of a protective tariff or by the prohibition of the importation of German dyes. Once this most essential part of the scheme is put into operation, or a guaranty secured that it will take effect when circumstances indicate its desirability, the next step is to organize and develop the existing British sources of supply, utilizing to the full the scientific forces of the country, which are not only ready but anxious to lend their aid.

The latest proposition to meet prospective competition is relatively simple and certain of accomplishing the purpose, although bearing all the earmarks of a "war measure." It is formulated as follows:

In the present scheme they have endeavored to nationalize the dye industry by helping to make the dye consumers their own producers. One further step along the lines of the present procedure will make the dyers masters of the situation. Let the government do for artificial dyes after the war what they are doing for natural dyes during the war. Let them hold option of purchase of all foreign dye imports or transfer it to the new concern, allowing it control of the dye trade as well as the national dye production. Then it could buy when favorable conditions presented themselves, producing the while, and selling either foreign purchases or home production at regulated prices as the demand arose at home or abroad.

Thus far the British Government has given no assurance of any definite plan by which the new industry is to be insured absolutely against the danger in question. There is, however, a growing conviction that some effective measure will be adopted before the time approaches for the cessation of military warfare and the beginning of industrial warfare.

The British Government makes an annual grant of $50,000 for the next 10 years, to be expended under the direction of the new company in furthering technical education. Presumably it will be devoted to training up color chemists in the universities and schools of science.

Acknowledgment is freely made that it is a most frugal allowance, but it is the most that the government felt warranted in promising at present in view of the vast military outlay.

It is generally conceded that the sum is totally inadequate when the conditions of the problem imperatively require a most generous outlay to equip promptly the necessary corps of young chemists. It is pointed out that there are over 1,000 highly trained chemists in the German color factories.

The following is a list of the British firms now producing artificial dyestuffs:

Read, Holliday & Sons, Huddersfield.
Clayton Aniline Co., Clayton near Manchester.
Brooke, Simpson & Spiller, Atlas Works, London.
British Alizarin Co.
John Dawson & Co., Kirkheaton Color Works, Huddersfield.
Levinstein (Ltd.) Vale Works, Blakely near Manchester.
Clauss & Rée, Manchester.
Robert Dale & Co., Manchester.
United Alkali Co., Liverpool.
Fernhill Chemical Works, Bury.

The four first mentioned are of considerable size. Several on the list have been more or less under German control in the past.

According to the Textile Mercury of Manchester, England, the members of the British Felt Hat Manufacturers' Association have issued an intimation to the trade to the effect that owing to the difficulty and cost in procuring dyeing materials they are unable to guarantee exact shades and penetration or to guarantee colors to be fast. The circular adds: "Our regret to inconvenience the trade is accentuated by the fact that although in many cases the cost of dyeing materials is increased by several hundred per cent, yet it is impossible to continue on lines as before."

"FIBROX."*

By E. WEINTRAUB.

Fibrox is the name given by the author to a fibrous material of the composition of silicon oxycarbide. The name is to suggest the remarkable structure of the material.

Amorphous silicon oxycarbides have been prepared before and even fibrous materials of that composition in very small quantities and in a more or less accidental manner.

The first to have prepared compounds containing silicon, carbon and oxygen were Schuetzenberger and Colson. They found in the year 1881[1] that crystallized silicon heated to a white heat in an atmosphere of carbonic acid absorbed that gas and was converted into a greenish white mass, which, after purification by means of potassium hydroxide and hydrofluoric acid, left a greenish powder which corresponded approximately to the formula SICO. The re-action according to them is

$$Si_3 + 2CO_2 = SiO_2 + 2SiCO.$$

The same substance was formed more slowly at a higher temperature by the direct combination of silicon and carbon monoxide. In the year 1882[2] Colson prepared by other methods, which are of no further interest in this connection, other silicon oxycarbides, and found in particular that by passing a *stream* of carbon dioxide over silicon at high temperature carbon monoxide is evolved and a silicon oxycarbide to which he attributed the formula $Si_4C_4O_2$ is formed.

These silicon oxycarbides of variable composition were all amorphous powders, unattackable by boiling caustic solutions and hydrofluoric acid not readily oxidized at high temperatures by oxygen, but decomposable by a mixture of chromate of lead and litharge.

Schuetzenberger and Colson succeeded also in preparing in minute quantities a fibrous material, and perhaps it will be of interest to quote their words:[3] "One to two grams of silica is introduced into a crucible of gas-retort carbon and covered by a disc of gas-retort carbon furrowed on its upper surface. In these furrows are placed several decigrams of silicon crystals, and the whole is covered with the ordinary lid. The whole is enveloped in titaniferous brasque and heated an hour and a half to reddish whiteness. The silicon is in large part converted into a greenish white oxycarbide, and very curiously a cylindrical column of greenish white oxycarbide, very light and porous, spread out above and below, runs from the center of the furrowed disc to the center of the lower side of the lid."

Mülhauser,[4] in making carborundum from coke, sand and salt, found between the layer of amorphous carborundum and the mixture of unattacked material a fibrous material. He describes it as grayish-green in appearance, the fibres being as long as two centimeters. The amount of substance he had was not sufficient for a carbon determination, and from the determination of silicon and aluminum he attributed to the substance the formula $AlSi_2C_7$.

In 1897, C. Kohn[5] described an accidental product of the carborundum furnace observed at the Carborundum Company's plant at Niagara Falls:

"One other product of the furnace is worthy of note. Tiny, feathery tufts are often found sticking to the carborundum crystals and occasionally the same product is found in larger quantity in the inner parts of the furnace in the form of pale greenish-yellow masses excessively light and extraordinarily like a fungus in appearance. On one occasion a piece quite 18 in. long, about 4 in. broad and 2 in. thick was obtained. At first this was regarded as volatilized silica but it is really carbide of silicon in an extremely fine state of division."

It is impossible from this distance to tell what the material described by Kohn was, but I am inclined to believe that this material and that found by Mülhauser were similar, and were a fibrous form of silicon oxycarbide.

Further observations on silicon oxycarbide were made in the Carborundum Company's plant, and in 1903 patents were issued to Acheson[6] on amorphous silicon oxycarbide, called by him Siloxicon. By heating carbon and silica in appropriate proportions in a furnace of the carborundum furnace type he produced compounds of a variable composition, such as Si_2C_2O and Si_7C_7O. The products are described as amorphous powders, very refractory, indifferent to all acids except hydrofluoric, by which they are attacked but slowly, resisting the action of hot alkaline solutions and capable of being molded into form and fired to yield a coherent mass.

In June, 1912, a patent was issued[7] to Tone on the manufacture of a fibrous silicon oxycarbide in the carborundum furnace under such conditions that a condensation product containing silicon, oxygen and carbon was formed. The material is described as containing on an average of 49.95 per cent silicon, 43.6 per cent oxygen, 6.45 per cent carbon, as having a real density of about 2.3 and an apparent density of 0.15, and its possible value as a heat insulating material is recognized. This material of Tone is distinguished from Fibrox by its high apparent density (about twenty to fifty times that of Fibrox), its high real density, and a lower carbon content. It is doubtful whether Tone ever succeeded in getting his material in quantities or in a regular way.

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*Paper presented at the 27th General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22-24, 1915

[1] C. R. Vol. 92, p. 1508.

[2] C. R. Vol. 94, p. 1710.

[3] "Si dans un creuset en charbon de cornues on introduit de la silice (1 à 2-gr.) que l'on recouvre d'un disque de charbon de cornues creusé en coupelle sur la face superieure on place quelques décigrammes de cristaux de silicium dans cette coupelle; si enfin apres avoir fermé le creuset avec son couvercle tourné on enveloppe le recipient de brasque titanifere et si on chauffe une heure et demie au rouge blanc, on constate que le Silicum est en grande partie converti en oxycarbure blanc verdatre et fait tres curieux, une colonne cylindrique d'oxycarbure blanc verdatre tres leger et poreux, épanouie en haut et en bas reunit le centre de la coupelle au centre de la paroi inferieure du couvercle."

[4] Z. f. anorg. Chemie, 1894, p. 119.

[5] J. of the Soc. of Chem. Ind., 1897, p. 866.

From my own experience I conclude that Fibrox is the result of a very slow growth, for which the conditions of the carborundum furnace are very unfavorable.

All these previous attempts beginning with the work of Colson down to the work of Tone were unknown to me at the moment when I started the work on Fibrox.

This work has originated from some accidental observations made in the Lynn factory. In melting silicon for the manufacture of silicon resistance rods, the formation of a fuzzy material on the top of the silicon was noticed. My attention was attracted to this, and recognizing the possible value of this material as a heat insulator, I decided to start an investigation to find out the conditions of formation of the material.

PREPARATION OF FIBROX.[8]

The different steps by which the factors essential to the production of Fibrox were discovered would possibly make interesting reading, but for the purpose at hand it will be sufficient to describe the final process adopted.

A muffle (or pot) of a material capable of withstanding a temperature of 1,400°-1,500° C., having its bottom covered with a layer of silicon pieces, is heated in a gas furnace to the temperature of incipient melting of silicon. A muffle of Dixon graphite clay-lined has proved to be suitable. The ends of the muffle protruding outside the furnace are luted on to the muffle in a gas-tight manner. *It is essential that a catalytic agent be used.* One such agent is calcium fluoride.

After a run of a few hours the muffle is found filled completely with Fibrox, which is removed and the operation repeated. It is only necessary from time to time to break up the slag which forms on the surface of the silicon and to add some fresh fluorspar or other catalyzer.

It is obvious from the process described that Fibrox is a product of slow and quiet growth, and from its composition it must be formed when silicon vapors and carbon dioxide or carbon monoxide react. The silicon vapors come from the silicon. The carbon dioxide comes from the combustion gases of the furnace. One has, therefore, to picture to himself the oxide of carbon slowly diffusing through the pores of the vessel and reacting with the silicon vapors. *This slow interpenetration of the reacting gases through a permeable wall is an important feature of the process and is essential if the finest structure is to be developed.*

The fluorspar or other catalyzer used has most probably the function of keeping the slag (silica?) in a sufficiently soft condition to allow the silicon to "seep" through it and expose a clean surface from which the silicon vapors can freely escape.

At the temperature of the incipient melting of silicon, which is used in this method of manufacture, carbon monoxide does not react appreciably. This was proved by heating the crucible in a furnace, the atmosphere of which was rich in carbon monoxide but poor in the dioxide. In one case the muffle was imbedded in charcoal. In another, the muffle was heated in an electric resistance furnace, the resistor of which was either carbon or carborundum. In neither case was the formation of Fibrox observed except in very minute quantities.

The experiment was then varied by letting carbon dioxide penetrate through the pores of the cover of the crucible either by admitting carbon dioxide into a chamber surrounding this cover or by placing a decomposable carbonate into the chamber. The formation of Fibrox was then proceeding in a normal way.

At *higher temperatures* carbon monoxide is capable of reacting with silicon vapors, producing a variety of Fibrox. This was shown by using a special type of electric furnace in which silicon was made to boil by passing current through it and carbon monoxide admitted. The product obtained, while similar to Fibrox, does not have as fine a structure as the gas-furnace product, is much heavier and is a poorer heat insulator.

PROPERTIES OF FIBROX.

Structure: The most remarkable thing about Fibrox is its physical structure. In order to appreciate the exceptional properties of the material, one must see it.

Fibrox is a soft, resilient, fibrous material; after gentle compression it returns to its original shape; it can be cut into plates, sheets and rings which are self-supporting.

The material is an agglomeration of exceedingly fine fibres. The diameter of the fibres is in average *about 0.6 micron, or about the wave length of yellow light.* Some fibers are undoubtedly smaller and probably approach 0.3 micron.

Density: The apparent density of the material, while varying with the circumstances, is usually between 0.0025 and 0.0030. In other words, it weighs only about 2½ to 3 grams per liter. The real density of the material varies with its composition. When the composition corresponds nearly to the theoretical silicon oxycarbide SiCO (about 21 per cent of carbon), the real density is 1.84.[9] As the carbon content diminishes the real density increases up to about 2.2, or nearly that of silica. From the real and apparent density, the actual volume occupied by air is figured out to be over 99.5 per cent and in the best cases equal to 99.9 per cent and that of the solid material is only between 0.5 to 0.1 per cent.

Heat Resistivity: The remarkable physical structure of Fibrox would make one expect it to be an exceptionally good heat insulating material. Measurements for which I am indebted to Mr. Randolph of the Heating Device Laboratory of the General Electric Co. have shown that Fibrox is the best heat insulating substance known.

For the temperature interval of 100° to 15° a long-fiber dark-green sample of Fibrox compressed to a

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[6] U. S. Patent, No. 722,793.

[7] U. S. Patent, No. 1,028,303.

[8] Most of the experimental work was carried on by F. Kroner.

[9] Determined by H. Rush, of this laboratory.

density of 0.767 lb. per cubic foot or 12.3 grams per liter has a resistivity in degrees per watt, per inch cube, $R' = 1,675$, or per cm. cube $R = 4,200$.

A comparison with other materials will be instructive. For wool at a somewhat higher density of 0.955 and the same temperature interval R' (in. cube) = 802 (R/cm. cube = 2,000) and at a density of 3.4 $R' = 1100$ (R/cm. cube = 2,700). Wool has to be compressed to a density of 12 pounds per cubic foot or more than 15 times that of Fibrox to get the same value of heat resistivity.

Eiderdown reaches a value equal to that of Fibrox at a density of 5, or more than 6.5 times the density of Fibrox.

Among the inorganic heat insulators, Monox has at a density of 6.18, $R' = 1,000$ ($R = 2,500$) and "Elephant Ear"[10] at a density of 8.4, $R' = 1,100$ ($R = 2,700$).

It will be seen that by its value of heat resistivity Fibrox stands in a class all by itself.

The heat insulating value of Fibrox is smaller at higher temperatures. The specimen referred to above (density 0.767) gave the following values, the lower temperature being alaways 15° C.

T	R′ in. cube.	R cm. cube.
100 degrees	1,675	4,190
200 degrees	1,320	3,300
300 degrees	1,050	2,625
500 degrees	878	2,195

But even so, Fibrox is also superior at high temperatures to the other known insulators which can at all be used at those temperatures. To compensate for the drop in the heat insulating value of Fibrox at higher temperatures, it would be necessary to use it at a somewhat higher density, a density which is, however, low as compared to that of other materials.

The effect of the density on the heat resistivity of Fibrox at temperatures of 200° and 500° is shown by the following table:

		Thermal Ohms	
Density.	Temp.	R′ in. cube.	R cm. cube.
0.231	200	950	2375
0.231	500	520	1300
0.412	200	1200	3000
0.412	500	605	1510
0.767	200	1320	3300
0.767	500	878	2195
1.27	200	1460	3650
1.27	500	987	2470
1.98	200	1590	3975
1.98	500	1000	2500

Taking the last value, we see that at the temperature of 500° C. and a density of about two pounds per cubic foot, Fibrox has a resistivity equal to that of Silox, Monox or Elephant Ear at a density averaging about 6 or 7 pounds per cubic foot.

In many heating devices the negative temperature co-efficient of heat resistivity is very desirable but in cases where very high values of heat resistivity at high temperatures are desired, I have suggested the following arrangement. It is probable that the negative temperature co-efficient of heat resistivity of Fibrox is due to the transparency of Fibrox for long heat waves which, being much larger than the diameter of the Fibrox fibres, pass around these through the air which is the main constituent of Fibrox agglomerate. To overcome this it would, therefore, be only necessary to break up the layers of Fibrox by means of absorbing or reflecting walls which would transform the heat waves into molecular heat of lower temperature.

Besides the high value of heat resistivity, all the other properties of Fibrox are such as to make it the ideal heat insulating material. It is perfectly permanent in air and is not hygroscopic.

It is self-supporting, and will not settle down even under the most severe conditions of transportation, etc.

It stands a higher temperature than other insulating materials, such as Monox or Elephant Ear. At temperatures above 1,000°, and up to 1,400°, Fibrox oxidizes in air but very slowly, so that only the layers nearest to the heating units gradually change into silica, a change which does little harm.

The heat capacity of Fibrox is very small, mostly on account of the very small mass of solid material. It is so small that very striking experiments can be made. For instance, a large piece of the material heated up in a Bunsen flame to incandescence can be grasped by the hand immediately after it is pulled out of the flame without any burning effect.

Electrical Conductivity: This is a most puzzling and almost paradoxical property of Fibrox. Fibrox, the best heat insulator, is a relatively good electrical conductor with a conductivity comparable to that of electrolytic solutions.

In making conductivity measurements it is important to secure good contacts and to avoid any sparking at the contacts. If the experiments are carried out in air, the local high temperature due to sparking at the contacts causes oxidation of the contact layer of Fibrox, and the silica film formed acts as an insulator. If due care is exercised and especially if alternating current is used, good measurements can be secured in air. In hydrogen and in carbonic acid or carbon monoxide good results are obtained a little more readily, although sparking must be avoided as much as possible to prevent disintegration, decomposition and pitting at the contact surface.

The following table gives a set of measurements carried out in an atmosphere of hydrogen. The piece had a cross-section 2.7x1.8 cm. and a thickness between the copper disc electrodes of 2 cm. No compression was used. The apparent density of the material was 3 grams per liter. The table below gives (1) the voltage across the piece of Fibrox, (2) the amperes and (3) the resistance.[11]

Volts.	Amps.	R.
8.7	0.05	174
12.1	0.10	121
16.7	0.18	93
21.0	0.35	61

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[10] U. S. Patents, 1,072,413, 1,072.414.

[11] Measurement by A. E. Hibschman, of this laboratory.

28.6	0.71	40
46.0	1.14	31.5
40.5	1.66	24.5
42.0	1.92	22.0
43	2.32	18.5
46	3.20	14.3

The specific resistance per cm. cube at the low current is about 360 ohms. When the piece carried 3.2 amperes, and had a temperature of about 800° C., the resistivity dropped to 30 omhs.

From this the specific resistance of the Fibrox *material itself* at or near ordinary temperature would be less than 1 ohm per cm. cube, and at 800° C., less than 0.1 ohm.

Compression of the Fibrox without destroying its structure increases the conductivity, but if the Fibrox structure is destroyed the conductivity disappears. In other words, each transparent fibre of Fibrox is a good electrical conductor.

The conductivity of Fibrox varies with its composition and appears to increase with the carbon content.

PRODUCTION OF PYRITE AND SULPHURIC ACID IN 1914.

PRODUCTION OF PYRITE.

The production of pyrite in the United States in 1914, according to W. C. Phalen of the United States Geological Survey, was 336,662 long tons, valued at $1,286,084. There was a decrease therefore in 1914 of 4,676 long tons in quantity, or slightly more than 1 per cent, and of $2,738, in value, or but one-fifth of one per cent.

Virginia is the leading state in both production and value. The output of this state diminished slightly in 1914 as compared with 1913. The output in California showed a slight gain. There was a substantial gain in the production in New York, which though ranking third among the states in production stands second in value. In Illinois, where pyrite is a by-product obtained in connection with coal mining, the output more than doubled compared with 1913. In Wisconsin there was a decreased production. In Georgia there was a slight increase. In both Ohio and Missouri there was a decline in production, and in Indiana, where, as in Illinois and Ohio, the pyrite is obtained in connection with coal mining, there was a slight increase as compared with 1913.

PRODUCTION OF SULPHURIC ACID FROM COPPER AND ZINC SMELTERS IN 1913 AND 1914, IN SHORT TONS.[a]
(Reduced to 60° Baume acid.)

Source.	1913 Quantity.	1913 Value.	1913 Price per Ton.	1914 Quantity.	1914 Value.	1914 Price per Ton.
Copper smelters	336,019	$2,205,627	$6.56	348,727	$2,215,690	$6.35
Zinc smelters	296,218	2,140,645	7.23	411,911	2,974,603	7.22
Total	632,237	$4,346,272	$6.87	760,638	$5,190,293	$6.82
Total acid reduced to 50° Baume	790,296	....	.....	950,798	....	.....

[a] The acid reported to the Survey includes strengths rated at 50°, 53°, 55°, 60°, and 66°Baume, and a small quantity of electrolyte and oleum. All strengths, with the exception of the electrolyte, have been reduced to both 50° and 60° Baume, as given in the table.

The imports of pyrite for consumption during the calendar year 1914 were 1,026,617 long tons, valued at $4,797,326. These figures show a notable increase compared with the imports of 1913, which were 850,592 long tons, valued at $3,611,137. The increase in imports in 1914 amounted to 176,025 long tons, and in value to $1,186,189.

PRODUCTION OF SULPHURIC ACID.

According to actual returns for the year 1914 the production of sulphuric acid in the United States was 3,762,417 short tons of 50° acid, valued at $24,163,331. This is exclusive of 21,993 short tons of fuming acid, valued at $316,596, but the figures given above include by-product acid—that is, acid obtained in the smelter industry. The acid producted at copper and zinc smelters in 1914 amounted to 950,798 short tons of 50° acid, valued at $5,190,293. The entire production of acid by grades is tabulated below:

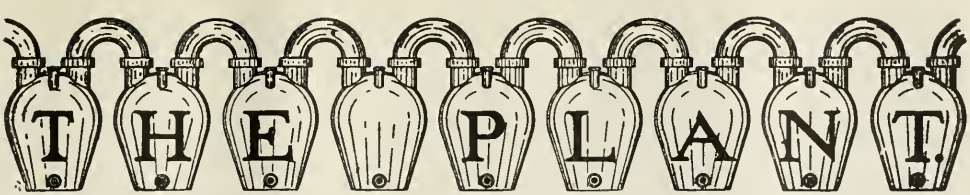
PRODUCTION OF SULPHURIC ACID IN THE UNITED STATES IN 1914 BY GRADES, IN SHORT TONS.

Grade.	Quantity.	Value.	Price per Ton.
50° Baume	1,628,402	$ 9,712,056	$ 5.96
60° Baume	551,955	3,376,242	6.12
66° Baume	916,192	10,509,471	11.47
Other grades	65,890	882,158	13.39
Total	3,162,439	$24,479,927	$ 7.74
Total reduced to 50° Baume acid	[a]3,762,417	[a]24,163,331	6.42

[a] Exclusive of 21,993 short tons of fuming acid valued at $316,596.

The above figures are final so far as the Survey's present information goes but are subject to change if necessary when the printed report is issued. The changes, if any are made, will be slight.

In the manufacture of acetylene gas (from calcium carbide and water) considerable quantities of so-called carbide slime are always left in the apparatus. The slime is a waste product, no means of utilizing it having been known heretofore. In view of the large increase in the consumption of acetylene since the outbreak of the war, the report of R. Schumann on the possible utilization of carbide slime, published in the Chemiker-Zeitung, will be of special interest. The material could not be used as fertilizer, salts of phosphorus being absent, but might be used as water purifier when of a certain composition. The experiments with the employment of carbide slime as building material yielded the best results. When mixed with 40 per cent of building sand, the carbide slime formed a usable mortar which set well and bound the bricks firmly. This new building material will be thoroughly tested by further experiments.



THE MANUFACTURE OF CONDENSED MILK, MILK POWDERS, CASEIN, ETC.*

By R. T. MOHAN.

As early as 1810 an English patent was granted to De Heine covering the evaporation of part of the water from milk, and its preservation with cane sugar. Other early English patents on condensed milk were granted to Newton in 1835, Grimway in 1847, De Lignac in 1847, and in France to Appert in 1827. The first patent for a vacuum pan for evaporating milk was granted, I believe, to Green in England in 1813 (Eng. Pat. 3754).

The object of these early inventors is clearly shown in Newton's English patent No. 6787, 1835, which reads:

> For preparing animal milk so that it may be preserved for any length of time with its nutritive properties, and capable of being transported into any climate for domestic and medicinal purposes; this being effected by adding to the milk a certain amount of sugar, and evaporating it by any suitable means, using only a gentle heat to quicken the operation. It may be brought to the consistency of cream, honey, or soft paste, or even into dry cakes. Cocoa, coffee, or tea may be evaporated with it.

The first instance of the successful manufacture of condensed milk on a commercial scale in America was in 1856 by Gail Borden, founder of the present firm of Bordens (U. S. patent 15,553 in 1856; English patent 509, 1856). Up to the year 1861 there was little demand for condensed milk, but during the civil war a great demand was created, and from that time on it has steadily increased.

The Anglo-Swiss Condensed Milk Co. was started by U. S. Consul Page, of Zurich, Switzerland, who first made the product in 1865, and in 1866 incorporated the Anglo-Swiss Co., which now produces over 80 per cent of all the condensed milk manufactured in Australia and Europe.

Milk was first preserved by sterilization in 1856, and unsweetened concentrated milk, or what is now known as evaporated milk, was first successfully manufactured in Highland, Illinois, in 1885.

The U. S. Consul Report of 1909 shows a production of 214,518,310 lbs. of sweetened condensed milk, and 280,278,234 lbs. unsweetened evaporated milk, increase of 8 per cent and 154 per cent respectively over 1905. The 1913 output in the United States amounted, I am told, to about 250,000,000 cans of sweetened and about 390,000,000 lbs. evaporated.

The milk supply for the condensing must be ample for the factory's capacity, and must be of the highest quality. It is under the rigid inspection of the factory, and constant inspection is also conducted of the herds, pastures, barns, and dairies. Rigid instructions are enforced as to cleanliness of the animals and dairies. No feeding or other operation which would raise dust is allowed for one hour previous to milking. Strict instructions are issued against the use of certain foods such as turnips, garlic, etc., and only limited amounts of ensilage are allowed. Immediately after milking the milk is cooled and aerated by running it over block tin coils through which cold brine or water circulates, and then stored in a cool place till brought to the factory. Each can as delivered at the factory is opened by the receiver, who is able to detect any undesirable odor in the milk. In addition to the flavor, the temperature is noted. Tests are also made for acidity, any milk above 0.2 per cent being usually refused. As the farmer is usually paid on the basis of percentage of fat a small sample is taken each day and tested for fat, or sometimes the test is made on a composite sample of a week's delivery, the sample being preserved with mercuric chloride.

It is customary to make frequent bacteriological tests on the supply from each farmer. A good practical test for the number of organisms present in the milk is the reductase test which is based on the fact that normal cow's milk has the power of decolorizing certain dyestuffs, the time of decolorization (reduction) depending on the number of micro-organisms it contains. The test is conducted as follows: 1 c.c. of methylene blue solution is mixed in a glass tube with 10 c.c. of the milk to be examined, 2 c.c. of paraffin oil is floated over it to exclude air, and the tube is kept at about 115° F. (46° C.). If the dye is decolorized within one hour the milk is regarded as very bad from a hygienic standpoint; if decolorized within 3 hours it is of second quality; if the color persists for more than 3 hours the milk is good.

Another test depends on the decomposition of hydrogen peroxide by an enzyme present in milk, known as catalase, the catalytic power of which is increased by the bacteria present. This method has not come into general use in Canada.

To determine the nature of the bacteria, so-called "fermentation tests" are applied. The best known of these is the "Wisconsin curd test," in which a pint of milk is heated in a sterilized jar to about 98° F., 10 drops of standard rennet extract is added, and the jar is closed and incubated for about eight hours at 98°

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*From Journal Society of Chemical Industry.

to 102° F. The jar is then opened and the odor observed, the curds are cut with a knife, and the appearance is noted. Good clean milk contains practically no organisms but the lactic acid bacteria, which produce no gas and no bad odors, and the curd formed, therefore should have only an occasional irregular hole. Milk produced under insanitary conditions will produce more or less gas, and the curds will be full of large irregular holes.

Another "fermentation test" is conducted by incubating samples of the milk in sterilized tubes at about 100° F. After twelve hours the samples are examined, and the bacterial content of the milk is judged by the character of the curd, etc.

The milk after weighing is poured through a large strainer and run into large enameled vats, fitted with stirrers, on the floor below. The room in which these vats are placed is kept as cool as possible. The treatment of the milk from now on depends on the product to be made.

Condensed Milk.—The Canadian standard is not less than 28 per cent of milk solids, and not less than 7.7 per cent of milk fat. The last inspection of milk made by the authorities and recorded in Bulletin 257, Inland Revenue Department, shows that the product on the market complies exceptionally well with this standard.

The fresh milk is drawn from the receiving vats into large copper vats known as fore-warmers, where it is heated after addition of the requisite amount of cane sugar. Some of the fore-warmers are heated by copper jackets, while others depend on live steam from an open pipe; the latter method introduces some condensed water from the steam, but the amount is very small. The amount of sugar added varies from 16 to 19 lbs. to 100 lbs. of raw milk. In some cases the sugar is added to the whole quantity of milk before it goes into the pan, whilst in others one-half or three-quarters of the milk is run in, and the sugar added to remainder. The temperature to which the milk is heated before it goes to the pan also varies in different factories. These variations by different operators are mainly directed towards overcoming crystallization in the finished product.

The milk is now sucked into the vacuum pan, and the "condensing" operation begins. The concentration is carried out at a vacuum of about 28 in. and a temperature about 140° F. The vacuum pans used are single type evaporators made of copper, round at each end, with straight sides. They are heated by a steam jacket at the bottom and also internally by large coils and are connected to a water-jacketed condenser.

The "condensing" takes about two hours. Samples are drawn off at frequent intervals through a double sealed test cup. The consistency is tested by means of hydrometers, the end point being 35° to 36° B. More often, however, the sample is cooled to 70° F., and the appearance and the way the milk "strings" are noted. The operators get quite expert in judging the concentration of condensed milk in this way. As soon as the right consistency is attained, the valves are opened, and the finished product is run into ordinary milk cans (about 14 gallons), which are then placed in a shallow iron tank through which cold water circulates; here they are stirred and cooled, to make the product smooth and free from lumps. The tanks are provided with a series of cam wheels driven from a central shaft, and so constructed that the milk cans fit rigidly on them. A stationary wooden paddle is placed in each can, and as the cans revolve the milk is stirred and cooled. After cooling, the syrupy product is filled into cans and sealed. This product is not sterilized, preservation being dependent on the low percentage of moisture present and the absence of air in the cans. Table I shows the average composition of the product compared with that of other evaporated milk powders. If properly made and kept airtight, it keeps for several years. It contains too much sugar for use as an infant food.

The product obtained as outlined is made from whole milk and complies with the standard in every way. A skim milk product is also made, but this is always sold as "skim condensed milk." It is manufactured in the same way. (See Table I for composition.)

TABLE I.—AVERAGE COMPOSITION OF CONDENSED MILKS.

	Solids. %	Ash. %	Fat. %	Protein. %	Lactose. %	Cane sugar. %
Condensed whole milk	72.6	1.6	10.0	8.0	12.0	41.0
Condensed skim milk.	70.0	2.0	1.0	10.5	14.5	42.0
Evaporated milk	26.3	1.6	7.9	7.7	9.1	....
Whole milk powder...	96.3	5.6	26.8	32.0	31.9	....
Skim milk powder ...	91.7	6.9	1.7	33.8	49.3	....

The greatest difficulty in the manufacture of condensed milk is to prevent "sandiness" due to crystallization of the lactose or cane sugar. A decrease in concentration to prevent this is impossible, as the successful keeping of the product depends on its having less than 30% of moisture, and to effect this the sugar must be added in proportion to give about 41% cane sugar. Over concentration and the use of too much sugar increase this sandy condition, but even with proper conditions of amount of sugar and percentage of solids, the lactose generally crystallizes. Each manufacturer seems to have his own method of overcoming this, and for this reason practice varies in regard to the method of and time of adding sugar, temperature, etc., in the pan, and the method of cooling.

On opening a can of condensed milk a layer of sugar is often found on the bottom. This may either be lactose which has settled, or cane sugar separated out owing to an excess being used. It is not detrimental to the product, except that the layer of milk above may not have enough solids to preserve it as long as it should be kept.

Another defect in condensed milk is so-called "buttons." On opening a can and pouring out the contents, one or more small lumps, varying in size from a pin-head to a bean, may be found attached to the side of the can. These are called buttons, and are not easy to explain. Some state that they are insoluble casein compounds formed by the action of the metals of the tin plate. The peculiar feature, however, is that they appear to grow. A satisfactory explanation for this trouble is yet to be given, I believe.

Occasionally a can of milk is found to be in a thick, gelatinous condition. This denotes too much milk solids and not enough cane sugar to make a syrup.

Other defects are rancidity, brown color, blown tins, or putrid odor. These conditions are due to too low percentage of solids to prevent bacterial changes, but at most they are rarely very marked until the milk is from 2 to 4 years old.

Thus it is seen that the manufacturer is faced with a difficulty as regards this product. Too little sugar may result in a gelatinous product or one that will not keep, whilst too much may cause excessive "sandiness" and separation.

Evaporated milk in Canada is defined as milk from which a considerable portion of water has been evaporated, and contains not less than 26% of milk solids, and not less than 7.2% of milk fat. This product therefore does not contain any added sugar, and is preserved by sterilization.

The milk is drawn from the receiving tanks into the forewarmers as before. Here it is brought to a boil, and then drawn into the pan and condensed as before, the operator drawing off an occasional sample, and testing the solids by hydrometer; when the proper density is reached the valves are opened, and the milks run over a series of cooling coils to prevent any rapid multiplication of organisms. From the coolers the milk runs into large copper vats, and a sample is tested for fat and solids. If these tests are satisfactory, the milk is next homogenized by breaking up the fat globules into very minute particles, and mixing them so intimately with the caseous matter of the milk that the cream does not rise to the top. It is claimed that homogenizing makes the milk more digestible. This process is accomplished by heating the milk to about 185° F., and forcing it through fine metal

$$S = 1.2F + 0.25\ (G - 1000) + 0.14$$

where S is the percentage of solids, F the fat, and G the specific gravity referred to water as 1000.

This gives good results, but only providing the fat has been determined accurately. It is obvious, therefore, that this method cannot be relied on entirely, and a quantity of the milk must be dried in vacuo and the residue weighed.

Ash is determined by burning the residue after evaporating the milk for solids. A temperature sufficiently high to votalize the chlorides must be avoided.

Protein is determined by the usual Kjeldahl method. The conversion factor is somewhere between 6.25 and 7.04. Provisionally the factor 6.38 is used.

Sugar.—In evaporated milk the only sugar present is lactose, and this is determined either by the polarimeter or by the gravimetric Fehling process.

In the condensed milk there is in addition to the lactose, a large percentage of cane sugar, and accurate results are difficult, co-operative work by the U. S. Association of Agricultural Chemists on the same samples having shown results for lactose varying from 9.74 to 12.05 per cent, and for cane sugar from 43.06 to 46.74 per cent.

The author has had a batch of milk prepared specially and from the weight before and after concentration calculated what the composition of the finished product should be. Invariably analysis showed a little more lactose and a little less cane sugar than there should be. It was thought possible that in the concentration there was a slight inversion of the cane sugar, making it appear to be lactose, but from experiments on mixtures of cane sugar, and lactose under similar conditions, it is certain that no change takes place.

Fat.—The determination of fat is by far the most important of all, and it is most difficult to get accurate and concordant results.

Table IV will show some results obtained by different methods. These results only deal with evaporated milk, as the condensed milk requires different treatment.

TABLE IV.—DETERMINATION IN FAT BY DIFFERENT METHODS.

Calculated fat.	Babcock.	Ether extraction.	Rose-Gottlieb.
%	%	%	%
7.25	6.9	6.83	6.87
7.98	7.7	7.46	7.78
8.74	8.1	8.13	8.26
9.14	8.7	8.33	8.90
9.70	9.1	8.67	9.40
10.35	10.3	9.13	10.07
Average— 8.86	8.46	8.09	8.55

The most reliable of these methods is the Rose-Gottlieb, but this averages 0.31 per cent fat low. The reason for these differences lies in the physical change which the milk has undergone during the concentration, homogenizing, and the sterilization. The casein has been invisibly precipitated into an insoluble curd, and each very minute particle of precipitated casein encloses a small amount of fat. In order, therefore, to extract all the fat it is necessary to dissolve completely the curd and liberate the fat. To this end many modifications and new methods have been proposed. With one or two exceptions these are not feasible.

In the ordinary Babcock method it is almost impossible to get a clear fat column; the acid appears to char the milk to a greater or less extent, depending on the concentration, season of the year, etc. The only rapid and accurate modification known to me is as follows: 4.5 grms. of the milk is accurately weighed into an ordinary Babcock test bottle, 17.5 c.c. of water added, and thoroughly mixed. Then 17.5 c.c. of concentrated sulphuric acid is added and mixed to dissolve the curd completely, and the mixtures centrifuged for five minutes. The bottles are filled to the neck with hot half-strength sulphuric acid, centrifuged again for 2 minutes, filled to the top of the graduations with boiling water, centrifuged for 1 minute, and the fat column read at 185° F. This reading multiplied by four gives the percentage of fat in the evaporated milk. The important points to be observed in this method to obtain a clear fat column and complete recovery of the fat, are correct dilution of the milk (4:1) before adding the strong acid, and the addition of hot half-strength acid in place of water after the first centrifuging.

TABLE V.—FAT BY MODIFIED METHODS.

	Calculated fat.	Modified ether extraction.	Modified Babcock.
	7.25	7.20	7.30
	7.98	8.00	7.98
	8.74	8.75	8.68
	9.14	9.20	9.20
	9.70	9.65	9.60
	10.35	10.40	10.40
Average	8.86	8.86	8.86

In the gravimetric methods it is also necessary first to remove the caseous matter, and then extract the fat. This is best done by the following method. A weighed amount of the evaporated milk diluted 4:1 is absorbed on a filter coil free from fat placed in an extraction cone, and without any preliminary drying extracted in a Soxhlet apparatus with 1 per cent acetic acid for two hours. This removes most of the protein matter. The cone is washed with hot water to remove the acetic acid, dried in an air oven at 100° C. for 6 to 8 hours, and extracted for 8 hours with ether in the ordinary way, and the extracted fat weighed.

The reliability of these modified methods is shown in Table V.

In determining the fat in condensed milk there is an added difficulty of the presence of cane sugar. For gravimetric estimation the modified ether extraction method described above is to be recommended. For a rapid centrifugal method, the following modification (by Leach) gives fair results: 15 c.c. of the 40 per cent solution of condensed milk is measured into a Babcock bottle, and enough of a copper sulphate solution is added to precipitate the proteins. The bottle capillary tubes under a pressure of about 250 atmospheres against a conical surface of agate or metal. Homogenized milk cannot be separated by means of a separator. From the homogenizer the milk goes to the filling machines, where it is run into cans, which are sealed and transferred to the sterilizer. The sterilizers are large circular iron drums, with a revolving frame work inside. The cans, in crates, are placed in compartments of the revolving framework. When filled, the door is closed, the retort nearly filled with water, and the temperature raised to the desired point and maintained for the necessary time, the can revolving all the time. The steam is then turned off and cold water run in till the cans are cold. The time and temperature are very important, and are very variable, so that this part of the work is in charge of experts. The factors governing the sterilization are acidity, solids, fat content, the season of the year, and size of cans. Milk of high acidity (over 0.4%) will easily curdle with high temperature, hence the reason for keeping the acidity as low as possible on the fresh supply. The effect of acidity on the milk is shown by Table II, made from actual experiment. The same milk was used in each instance, and the same temperature and time.

TABLE II.—EFFECT OF INCREASED ACIDITY ON MILK. FRESH MILK 0.17% LACTIC ACID.

Concentration.	Acidity.	Condition of Milk.
1.58 : 1	0.30	Not precipitated.
1.74 : 1	0.34	Not precipitated.
1.90 : 1	0.40	Not precipitated.
1.99 : 1	0.43	Not precipitated.
2.11 : 1	0.48	Small lumps of curd.
2.25 : 1	0.54	Large lumps of curd.

Milk of different seasons will stand different temperatures, fortunately the highest in the summer. The fresh milk varies in composition with the seasons, and hence the concentration also has to be varied to bring the product up to standard. Table III illustrates this:

TABLE III.—VARIATION IN CONCENTRATION WITH SEASONS.

	Solids in fresh milk.	Concentration.	Solids in condensed milk.	Condition of condensed milk.
June	12.68	2.00 : 1	25.38	Smooth—no separation or curdiness
August	11.75	2.21 : 1	26.01	
November	13.40	1.99 :1	26.62	

Note.—Lower concentration causes separation of fat, and higher causes curdy milk.

In most factories it is customary to make a trial sterilization on a small batch to see what temperature the milk will stand before it curdles. To do this a small sterilizer is built on the same plan as the large one, and holding half a dozen cans. The milk is sterilized at 235° to 240° F. (113°-116° C.) for about thirty minutes. The milk is next shaken to make it smooth and uniform. About four dozen cans are fitted into crates, and placed in a machine which has a very rapid oscillating motion for one to three minutes, depending on the milk. After shaking, the milk is stored in a warm place (practically a large incubator) for about three weeks prior to shipping. Any "leaks" or "swells" are then picked out, and the good cans are labelled, cased, and shipped.

This, therefore, is a product which is desirable from every standpoint, handled under sanitary conditions, and completely sterilized. It is a concentrated whole milk product containing no adulterants, and finds a ready use for general and for infants' feeding.

Absolute cleanliness is maintained in the factories. All pipes are cleansed daily with hot soda solution and then with live steam, and the vats, coolers, and vacuum pans are scalded, scrubbed and sand-papered every day.

Defects.—Swells, flat sours, and sweet curdling in evaporated milk are due to under-sterilization. Curdiness (other than sour curd) is due to precipitation of the curd as a hard mass under the action of the heat on a product of high solids and acidity. The hard grains sometimes found in the bottom of the cans consist of mineral matter, mostly calcium phosphate, precipitated owing to over-concentration.

Plain condensed milk is milk evaporated about 4:1, which is filled into barrels, and used within a day or so by ice cream manufacturers and confectioners.

ANALYSIS OF CONDENSED MILK.

Sampling.—In the evaporated or unsweetened variety there is little difficulty in getting an uniform sample from the can, as it is only necessary to stir it thoroughly. However, the condensed or sweetened variety presents a possibility of error, especially when the sugar has settled. The best method of sampling in this case is to transfer the whole contents of the can to a large mortar, and thoroughly grind and mix it; a 40% solution is then prepared and analyzed.

Solids.—For the sweetened condensed milk a quantity of the 40% solution is evaporated to dryness, in vacuo, or in a McGill oven (in which the product is dried in a current of air at 70° C.). Drying to a constant weight on a steam bath or in an ordinary air oven does not ensure accurate results, as the solids seem to retain a small proportion of the moisture with great tenacity, and if dried too long undergo chemical changes.

For the unsweetened or evaporated milk two methods are available, one by taking the specific gravity of the 40% solution and calculating the solids by formula, the other by evaporating and weighing. For taking the gravity hydrometers with special scales, and called lactometers, are used. The two most common are the New York Board of Health and the Quevenne lactometers. In Canada the former is used almost entirely. The formula used to calculate the solids is:

is then centrifuged, and the precipitated proteins carry the fat to the bottom of the bottle. The clear liquid above is then drawn off by means of a pipette having a wisp of cotton wool over the end to prevent any of the precipitate being withdrawn, and the remaining fat and protein is thoroughly mixed with water and again centrifuged. This operation is repeated until the sugar has all been removed; 17.5 c.c. of water is added to the precipitate, then 17.5 c.c. of strong sulphuric acid, and the operation continued as in the ordinary Babcock test. This method eliminates the trouble due to charring of the sugar, but still has the defects connected with the Babcock test when used for evaporated milk.

Milk Powders.—In making these the difficulty has been to produce a powder which when mixed with water would produce a fluid similar to milk in appearance, flavor, and physical properties. Many methods have been tried, and numerous patents granted, but, with one or two exceptions, there has been little success. The two most successful processes are by drying on steam-heated rolls, and by spraying the milk into a tower.

In the roller system, the milk is run on to steam-heated metal rolls, generally in vacuo. The dried powder is scraped off the rolls, and ground. The resultant powder, while fairly good, is not as soluble as it should be.

The spraying system has been more successful. The milk is first reduced in a vacuum pan to about one-fifth of its volume. It is then atomized into the top of a hot chamber, the moisture being removed while the fine particles of milk are falling to the floor. The dried product accumulates on the floor as a very dry flour, and needs no grinding. The powders produced by these spraying systems are excellent, and find a ready use with bakers, confectioners, etc. For composition see Table I.

These products are analyzed by making a solution the strength of ordinary milk, and analyzing this. All the difficulties mentioned for the analysis of evaporated milk are also met with in this product.

Casein.—When the milk supply is too heavy to be handled by the evaporators, it is usual to skim the milk, ship the cream into the cities, and prepare casein from the skim milk. The present uses of casein are numerous and increasing. They include paints, dressing for textiles, cements and mucilages, plastic masses, sizing for paper, food products (under trade names such as Sanatogen), and many others.

The casein content of ordinary cow's milk averages 3.2 per cent. It is easily precipitated by acids. Technically, it may be made by spontaneous souring of the milk, or more often by the addition of acids, as hydrochloric, sulphuric, or acetic acid; also by precipitation by rennet. Combinations of these methods are also used, the casein being sometimes dissolved in alkali and re-precipitated by another acid. Many patents cover the manufacture of this product, each one of which has its own special claims. The casein is washed and dried on trays, preferably in a vacuum drier. It is then ground.

The trade in America is controlled by two companies, the Union Casein Company, and the Casein Company of America, both of which manufacture many products from the raw material.

Those specially interested in casein and its compounds are referred to Robert Scherer's book on "Casein: Its Preparation and Technical Utilization."

Not infrequently the whey (after the separation of the casein by rennet) is evaporated down, and the lactose obtained. Processes similar to the manufacture of ordinary sugar are used.

THE PREPARATION OF FERTILIZER FROM KELP.*

By J. W. TURRENTINE.†

The term "kelp," formerly applied to the ashes of seaweeds, now has come to mean any of the brown marine algae. In general use its meaning has become restricted to the large and conspicuous sea algae of the Pacific coast. The so-called giant kelp of the Pacific coast may be defined as four species of the marine algae, whose botanical names are Pelagophycus porra, Alaria fistulosa, Nereocystis luetkeana, and Macrocystis pyrifera, named in the reverse order of their present economic importance. Only two of these, the latter two, at present should be considered in a fertilizer connection, as, of the former two, the Pelagophycus porra occurs in too small amount to be important, though it carries a very high proportion of valuable fertilizer ingredients, and the Alaria fistulosa is too low in potassium to merit treatment where the other kelps are available in sufficient quantity.

The Nereocystis is an annual whose seasonal growth attains an average of 50 feet. The rapid growtn necessary to reach such a size in a growing season connotes an abundant supply of the elements or compounds which enter into the plants' metabolism, and this, in turn indicates a large and constantly changing volume of the medium in which it grows. Thus it is found in localities of heavy surf or strong tideways. To maintain itself in position under these conditions it must attach itself firmly to the bottom. Therefore a rocky bottom is essential to the establishment of groves of the plants. To attach itself, the plant develops a "hold-fast," a root-like growth which tends to grow around and grasp the objects with which it comes into contact, thus anchoring the plant. Extending upward from the hold-fast is the stipe, a long, slender stem, tough and cord-like, which reaches almost to the surface of the water. Toward its upper end it gradually enlarges, becoming hollow, and culminates in a hollow bulb. This portion, being air-filled, serves to float the plant, and is called the pneumatocyst. The plant thus is lifted and held in the sunlight. From the top of the pneumatocyst develop two tufts or bunches of long, ribbon-like leaves, called fronds, which grow ten or fifteen feet in length and trail out in the tidal currents. The most interesting characteristic of the plant and a characteristic that distinguishes it from the other important kelp, the Macrocystis, is that almost the entire plant, on the basis of weight, lies on or near the surface, from the enlarged portion of the stipe upward. This fact has an important bearing on the harvesting of this species, as cutting the stipe a few feet below the surface severs practically the entire plant.

The Macrocystis, a perennial, reaches an average of 100 feet, and grows likewise in regions favored by a rocky bottom and a swift tideway or heavy surf. It attaches itself in the same manner as does the Nereocystis, which is characteristic of the kelps, but instead of a single stipe extending from the hold-fast, it develops a number, which gives the effect of a bushy or branching plant. The fronds are distributed along the entire length of the stipe. These reach a maximum of about three feet in length, and decrease in size as the upper or younger end of the plant is approached. A short section of stem connects the frond to the stipe and bears a pear-shaped enlargement which is hollow and serves as the pneumatocyst. The plant does not stop growing on reaching the surface, but a large portion of its length lies upon the surface, supported by its numerous pneumatocysts, and trails out in the tidal currents.

Reproduction by these species is by means of sporangia, small bodies which develop on the fronds in the case of the Macrocystis on the old fronds near the bottom, and which are thrown off to find lodgement and develop into new plants. As the Nereocystis is in effect an annual, its continuance is dependent on annual reseeding. While plants have been observed which have withstood the winter's cold and storms, thus appearing to be at least a biennnial, most of the groves are torn out by storms during the winter and are reformed during the following summer. In harvesting these groves, then, due precautions must be taken to leave enough plants for resporing, or to postpone harvesting until after the sporing season. In the case of the Macrocystis, it is probable that no such precautions need be observed.

In this connection it should be said further that only one harvesting per season of the Nereocystis is possible, since cutting that plant a few feet below the surface of the water, as pointed out, severs the entire growing portion. It is necessary then to await the new growth of the next season.

Such is not the case with the Macrocystis. Cutting that plant a few feet below the surface of the water severs only the upper part of the growing portion, possibly one-half, and does not kill the plant. On the contrary, there seems to be a certain stimulation in growth exhibited by a sort of "stooling effect"; while the old stipes slowly decay, fresh shoots appear, resulting in a thicker growth. It is estimated that after a cutting, a grove resumes its original condition after a lapse of 40 to 60 days.

DISTRIBUTION AND QUANTITIES.

On the Pacific coast of the United States the two commercially important kelps, Nereocystis and Macrocystis, characterize, respectively, the northern and southern stretches of that coast. While it is true that they are found together at certain places and that either one or the other occurs in thin fringes or patches along the entire length of the coast, the Nereocystis occurs in large and thick groves in the Puget

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*From The American Fertilizer.

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Sound region and the Macrocystis on the California coast, south of Point Sur, in southeastern Alaska large groves of both species occur; and in western Alaska, in the neighborhood of Kodiak Island and the mouth of Cook Inlet, the Nereocystis is found.

The important groves from the Mexican boundary to the Canadian line on Puget Sound, during the past three years, have been measured and mapped to scale; likewise, the important groves of southwestern and western Alaska have been surveyed.(¹) As a result of these three years' work, it is known definitely what the available quantities of kelp are on the various sections of the coast. Economically, the important groves group themselves around certain centers where there are harbors and where labor and transportation facilities are favorable. The natural centers are Puget Sound, Santa Barbara, San Pedro, and San Diego, on the coast of the United States, and Ketchikan and Kodiak, in Alaska.

The Puget Sound groves, it is estimated, can be made to yield 390,000 tons of wet kelp per year. The principal groves here, in convenient reach of Bellingham and Anacortes, is the Smith Island grove, which, it is calculated, would produce 100,000 tons per season. Other important groves lie near the American shore of the Straits of Fuca (85,000 tons) and the San Juan Islands.

Opposite Santa Barbara is a grove of approximately 3.9 square nautical miles, which would yield about 320,000 tons of wet kelp per cutting. Near San Pedro, extending from Point Fermin to Malaga Cove, are two groves of a joint area of 2.4 nautical square miles, which at a single harvesting should produce 194,000 tons of wet kelp. Near San Diego, north of Point Loma, likewise, are two groves of a combined area of 7.7 nautical square miles, from which could be harvested at one cutting about 633,000 tons.

In southeastern Alaska 70 square miles of kelp beds have been surveyed, carrying about 8,000,000 tons of wet kelp. These are distributed along a coast line of about 6,000 miles in a region of many islands and circuitous fiords and arms of the sea. While the length of the shore line, relatively speaking, is enormous, the actual distances from point to point are not great. Thus the entire area of this portion of territory is about 25,500 square miles, which is about the area of the states of New Hampshire, Vermont and Massachusetts.(²) Of the amount of kelp surveyed, groves containing 2,880,000 tons are regarded as easily available, the availability being estimated on the basis of quietness of water and freedom from rocks and other obstructions to navigation.

The kelp of this region has been grouped around eight centers, which are:

(1) Port McArthur, near the south end of Kuiu Island.

(2) Shakan Bay, on Summer Strait.

(3) Tyee, near Point Gardner.

(4) Duke Island, possibly inside the Vegas Islands.

(5) Saginaw Bay, at north end of Kuiu Island.

(6) Warren Cove, on Warren Island.

(7) Barrier Island, between Cape Chacon and Cape Muzon.

(8) Bay of Pillars, on Chatham Strait.

These points have been selected by Professor Frye from the viewpoint of both amounts of available kelp and convenience of harbor.

In this region, as well as in wetsern Alaska, large and heavy groves of Alaria fistulosa occur. This is a kelp which attains great size, but carries only a small proportion of potash. Its nitrogen content is correspondingly high, but not high enough to make it of equal commercial importance with the other two species.

The kelps of western Alaska so far mapped (by Prof. G. B. Rigg, of the University of Washington, during the summer of 1913) contain about 3,500,000 tons of green kelp, the estimate being based on the supposition that the kelp would be cut about 5 feet beneath the surface. The species included are both Nereocystis and Alaria. "Of this 1,251,200 tons are in beds of pure Nereocystis; 1,457,300 tons are in beds of mixed Nereocystis and Alaria."(³)

Large kelp beds are within easy reach of the harbors of Port Graham, Seldovia, Kodiak and Alitak, on Olga Bay.

COMPOSITION.

The composition of the kelps here is considered only from the point of view of their fertilizer value. In the following tables are given the respective composition of a number of samples of Nereocystis and Macrocystis, collected from various localities through a number of years and analyzed in the laboratories of this bureau. These tables are made up of results published elsewhere by the writer.(⁴) Lindemuth and Parker, (⁵) and Merz.(⁶) The samples may be regarded as average samples since they were collected only as representative of the groves distributed along the coast.

DISCUSSION OF RESULTS.

In these tables the potash is recorded as such, that is, as the oxide, the conventional manner of expressing the potassium content of fertilizers. It must not be understood that this is the form in which it occurs in the plant. When the plant has been incinerated at a low heat, so that all volatile organic matter has been driven off and only charcoal remains, and leached, potassium chloride is obtained. While it is not known definitely what compound of potassium exists in the living plant, it may be regarded as potassium chloride. In addition to the potassium chloride, sodium chloride

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[1] The groves of the Pacific Coast of the States were surveyed by Capt. W. C. Crandall, of the La Jolla Marine Biological Institute; those of Puget Sound and Alaska, by Professors T. C. Frye and C. B. Rigg, of the University of Washington.

[2] From the report of Prof. T. C. Frye, on the Kelps of Southeast Alaska, on file in the Bureau of Soils.

[3] Rigg, unpublished report on the Kelps of Western Alaska, in the files of the Bureau of Soils.

[4] J. Ind. Eng. Chem., 4, 1912.

[5] J. Ind. Eng. Chem., 5, 287 (1913).

[6] J. Ind. Eng. Chem., 6, 19 (1914).

is present in varying amounts, roughly equal to about one-third that of the potassium chloride. Also, there are small quantities of phosphoric and sulphuric acids, and calcium and magnesium. By lixiviation practically all of the soluble salts, principally of potassium and sodium, are removed. If the remaining charcoal then be burned, an ash remains which consists essentially of calcium and magnesium carbonate and phosphate. The percentage of ash varies from 3 to 12 per cent, the variation being determined by the part of the plant undergoing analysis. The stipe carries a much higher proportion of ash than the leaves or fronds.(7)

TAABLE I.—COMPOSITION OF NEREOCYSTIS.

Location.	K_2O. %	Iodine. %	Nit. %	Organic Matter. %
Fresh Water Bay, Puget Sound	18.04	0.23	2.26	51.13
	17.61	0.24	2.21	51.11
	31.62	0.25	1.21	33.15
	16.92	0.20	2.57	51.16
	17.05	0.24	2.71	51.67
	17.32	0.28	2.53	50.12
	16.20	0.19	2.54	52.14
	16.50	0.30	2.21	37.40
	16.72	0.20	1.46	39.02
San Juan County, Wash.	25.70	0.08	1.29	41.80
	13.30	0.15	2.52	61.50
	23.00	0.17	1.32	46.20
	16.20	0.15	2.32	35.30
Point Arena, Cal.	16.72	0.13	2.22	53.56
	20.62	0.15	2.25	51.42
Bay of Monterey, Cal.	16.96	0.20	2.15	57.25
	23.82	0.17	2.41	47.26
	21.70	0.18	1.58	50.20
Point Pinos, Cal.	19.40	0.12	1.70	53.00
	26.10	0.15	1.12	40.60
Cayucos, Cal.	20.83	0.24	1.93	47.86
Geese Island, Alaska	28.26	0.06	1.06	43.52
	15.44	0.14	2.27	56.26
Fort Graham, Alaska	24.69	0.06	1.15	40.50
	14.78	none	2.02	42.74
Pearse Canal, Alaska	12.74	none	2.87	60.50
	23.88	none	1.53	39.90
Between Tongass and Kanagunut Isle	15.12	0.07	3.06	55.56
	30.12	0.05	1.07	33.50
Gulf of Esquibel, Alaska	27.02	none	0.81	39.92
55° 37′; 133° 28′	19.63	none	1.04	49.28
Eagle Island, Davidson Inlet, Alaska	16.74	0.06	1.52	51.60
Wrangell Straits, Alaska	24.80	0.03	0.98	42.78
55° 54′; 133° 30′	28.76	none	0.59	32.66
56° 36′; 133° 57′	17.67	0.01	2.01	50.62
56° 12′; 133° 40′	20.12	0.06	1.85	48.56
56° 08′; 133° 54′	26.05	0.10	1.46	43.78
53° 36′; 132° 57′	21.61	0.09	1.65	43.50
57° 01′; 134° 34′	22.73	trace	1.54	55.56
Average	21.49	0.11	1.80	47.75

TABLE II.—COMPOSITION OF MACROCYSTIS.

Location.	K_2O. %	Iodine. %	Nit. %	Organic Matter. %
Low Point, Wash.	12.80	0.23	1.37	59.40
Neah Bay, Wash.	19.60	0.20	1.81	51.50
Piller Point, Cal.	17.26	0.15	2.18	58.14
	27.66	0.14	1.00	41.04
Santa Cruz, Cal.	16.44	0.24	2.16	59.80
Monterey Bay, Cal.	18.30	0.26	2.32	57.00
	12.38	0.18	2.11	68.80
Point Aulon, Cal.	23.00	0.32	1.83	51.20
Point San Luis, Cal.	8.62	0.14	2.35	68.26
Rocky Point	9.35	0.25	2.72	73.06
Point Conception, Cal.	14.17	0.24	2.15	62.95
San Miguel Island	16.40	0.29	1.54	50.60
Santa Cruz Island	17.40	0.32	1.57	49.40
Anacapa Island	12.60	0.26	0.95	64.40
Cape Quemada, Cal.	14.10	0.29	0.90	63.50
Goleta Point, Cal.	16.20	0.17	1.00	56.70
Point Las Pitos, Cal.	12.30	0.20	0.98	66.20
La Jolla Point, Cal.	13.60	0.38	1.04	64.40
Point Medanos, Cal.	13.40	0.23	0.74	62.90
Point Loma, Cal.	15.70	0.15	0.90	60.90
Bet. Duke Island and Bee Rocks, Alaska	11.49	0.06	1.08	67.34
56° 21′; 133° 36′	8.63	none	2.68	67.34
57° 13′; 133° 34′	6.92	trace	2.69	73.96
57° 01′; 134° 34′	7.30	none	2.19	73.24
55° 22′; 133° 16′	13.26	0.10	1.25	64.36
54° 58′; 132° 29′	22.48	0.30	2.64	49.02
Average	13.63	0.19	1.83	69.00

From the results of analyses recorded above the following generalizations have been made.

(1) No definite quantitative relations exist between the different constituents of kelp.

(2) The potassium content of Nereocystis is greater than that of Macrocystis.

(3) The potassium content of northern kelp is higher than that of southern kelp.

(4) There is no positive difference in iodine content between northern and southern kelps.

The following conclusions also seem justified:

(5) The proximity of the mouth of a fresh water stream has no appreciable effect on the potash and nitrogen content of kelp.

(6) There are no essential differences between the potash and nitrogen content of fronds and stipes.(8)

KELP AS A FERTILIZER.

In the British Isles kelp has been used as a fertilizer for centuries. So highly is it estimated that lands carrying kelp-harvesting privileges have been especially valued. In New England, also, kelp or seaweed has found favorable use as a soil amendment. In Alaska, especially on Kodiak Island, near the village of Kodiak, and in the neighborhood of Skaguay, it is used in like manner, on the former island particularly in fertilizing potatoes and in the latter region, truck gardens.

The Pacific kelps are markedly different from the seaweeds of the Atlantic coast, especially in the particulars of their very much greater size and their relatively enormous content of potassium chloride. It is these two qualities that give them especial importance as a possible source of fertilizer materials.

In the regions mentioned, kelp has been applied to the soil as a mulch, in its green state, or, better, after it has been cured by drying in the sun, or rotted by being allowed to stand in heaps.

Kelp has been harvested mechanically near San Pedro, California, and shipped in the crude, undried condition, to the ranches and orchards of that part of the state. As the green kelp, after draining, contains about 85 per cent water, its content of potash and nitrogen are about 2.6 per cent and 0.3 per cent, respectively. These values are obtained by calculating back from the values established on the dry basis to that of a content of 85 per cent water.

The manurial value of green kelp as compared with a number of other materials commonly used as fertilizers is brought out in Table III.[9]

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[7] For analyses of the various kelps of the Pacific Coast other than and including those of commercial importance, and for others of various algae of various parts of the world compiled from the literature, see Appen. P. of Senate Document, No. 190, 62d Congress, 2d Session.

[8] Cameron, "Kelp and Other Sources of Potash," J. Frank, Inst., October, 1913, p. 363.

The high content in water of the green kelp and its resulting low content in valuable constituents restricts its use to regions within easy reach of the points where it is harvested. For that reason, any scheme for the large-scale utilization of kelp as a fertilizer must be based on some method of concentrating its valuable constituents. Since all of these are either neutral or beneficial from a fertilizer point of view, it is necessary only to concentrate them by the removal of the water, or in other words, by drying. After an investigation of several years and a careful consideration of the nature of the raw materials involved, the value of the products obtainable and the costs of obtaining them, together with the demands of the fertilizer trade and the economic conditions existing on the Pacific coast, it appears that kelp, in the beginning at least, most advantageously can be prepared for the fertilizer trade merely by drying and grinding.

The product obtainable, as shown by small-scale operations, is a coarse gray powder of such a specific gravity that a cubic foot weighs 51 pounds. While it does not absorb moisture readily from the air, when wetted it swells and may become sticky and gelatinous.

In composition it would approximate closely the values obtained from the foregoing Tables I and II. The drying would not be quantitative; that is, a certain proportion of water would be allowed to remain, probably 7 to 10 per cent. Assuming the larger figure, the other values would be reduced proportionately, namely 10 per cent. The pulverized kelp, then, would contain 15.8 per cent potash and 1.95 per cent nitrogen. On the retail market of the Pacific Coast States, the prices of $1 per unit of potash and $3.30 per unit of available ammonia are obtainable. On this basis, assuming all the nitrogen available, the value of the kelp per ton is arrived at as follows:

15.80 per cent K_2O at $1.00	$15.80
1.96 per cent NH_3 at $3.30	6.47
Total value per ton	$22.27

In the wholesale market of the East, the prices are $0.65 per unit of potash and $2.85 per unit of ammonia, on the basis of which the value of the kelp would be:

15.80 per cent K_2O at $0.65	$10.27
1.96 per cent NH_3 at $2.85	5.58
Total value per ton	$15.85

TABLE III.—COMPARISON OF THE COMPOSITION OF WET KELP WITH OTHER MANURIAL PRODUCTS.

	Moisture. %	Nit. %	Potash. %	Phos. Acid. %
Horse manure[10]—				
Solid fresh excrement	.....	0.44	0.35	0.17
Fresh urine	.....	1.55	1.50	....
Stable manure[10]	73.27	0.50	0.60	0.30
Green alfalfa[10]	75.30	0.72	0.45	0.15
Cowpeas[10]	78.81	0.27	0.31	0.98
Street sweepings, Wash., D. C.[11]	.....	0.86	0.55	0.55
Wet kelp	85.00	0.30	2.50	0.20

From the analyses of the dry kelp it is seen that it is distinctly a potassic fertilizer and would enter the trade as a potash carrier. Since the present practice is to use the mixed or "complete" fertilizers, the kelp, if produced on a large scale, would find its market as a potash carrier to be mixed with phosphates and ammoniates to form the "complete" fertilizer.

For this purpose, it would enter into competition with other potash carriers, the German potash salts. These are, principally, kainite, a double salt of potassium and magnesium, $MgSO_4$, KCl, $3H_2O$, and "manure salts," a mixture of potassium, sodium, calcium and magnesium salts. Kainite, when pure, has a theoretical content of 18.9 per cent potash, but in the impure condition in which it is found on the market carries about 12.5 per cent potash. It sells for about $8.25 per ton. "Manure salts" vary widely in their potash content, but generally are of low grade and carry 16 to 20 per cent of potash. At present kainite, as such is disappearing from the market, being classified with "manure salts."

A comparison of the efficacy as a fertilizer of the potash in kelp and that in potassium salts of the general type used in mixed fertilizers has been made in the laboratories of this Bureau by Messrs. Skinner and Jackson.([12]) The two were applied to growing plants in equivalent amounts. The results showed that the kelp as a potassic fertilizer was quite as effective as the potash salts themselves. Since sodium chloride is found as a constituent of kelp, it has been suggested that its use on soils addicted to alkali might prove objectionable. In reply to this it should be said that the amount of salt actually added to the soil in the kelp is extremely small; in such amounts it has been shown to exhibit fertilizing properties, itself. Further, sodium chloride makes up but a small proportion of alkali, that being either sulphate of calcium or magnesium or carbonate of soda. If such an objection were valid, it would apply much more to the material now in use as potash carriers, the "manure salts," which, we have seen, contain soluble salts of both calcium and magnesium. In the case of the potash salts, the constituents other than potash have no value on a fertilizer basis and therefore are merely so much inert material on which transportations must be paid. The deleterious action of these in some soils would be undoubted if the fertilizers of which they form a part were used in very great amount. They are objectionable on the further score that they render the material of which they form a part hygroscopic, which property in moist air causes the fertilizer to cake. The ingredients of kelp other than potassic, it has been shown, are salt and organic matter, the nitrogen of which, rated as ammonia, adds materially to the market price of the product. The organic matter itself is of value, as contributing, to a small extent, to be sure, to the organic constituents of the soil, known by the indefinite term of "humus."

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[9] "Kelp and Other Sources of Potash," Cameron, J. Frank. Inst., October, 1913, p. 377.
[10] From Soils, by S. W. Fletcher.
[11] Analysis by J. G. Smith, Bureau of Soils.

PREPARATION OF DRY FERTILIZER FROM KELP.

Since the ingredients of kelp are either neutral or beneficial in their influence on plant growth, to prepare kelp for use as a fertilizer it is necessary only to convert it into a form in which it can be preserved and shipped. To accomplish this it is sufficient to harvest, drive off the water which it contains, and grind it to a coarse powder for bagging and mixing.

Kelp is being harvested by a machine which embodies the principles of the mowing machine or reaper used in harvesting agricultural products. The harvester actually in operation consists essentially of a barge over the end of which projects an adjustable frame, supporting an endless belt, tilted to form an incline plane. Across the lower end of the belt extends a horizontal cutting bar about 10 feet in length of the type used in the construction of reapers, which is supplemented at each end of two perpendicular knives. By this arrangement a swath may be cut through the kelp 10 feet in width and of a depth determined by the adjustment of the supporting frame. Back of the knives the belt, constructed of chains and netting, is operated in such a way as to catch the severed kelp and lift it upon the barge. Beneath the upper end of the belt is a chopper into which the kelp drops and by which it is cut into short lengths. From this it passes onto a short conveyor which loads it into a scow made fast alongside. The small barge carrying the cutter is moved along the side of the large scow so that the load of cut kelp is distributed evenly. To operate the moving parts of the machine a gasoline engine is provided. The barge and scow are pushed through the kelp groves by a launch, which serves also to tow them to the dock for unloading.

TABLE IV.—YIELD IN VARIOUS CONSTITUENTS TO BE EXPECTED FROM 1,000 TONS OF FRESHLY CUT MACROCYSTIS AND ALARIA.

	Macrocystis.	Alaria.
Wet tons	1,000	1,000
Dry tons	132	137
Tons K_2O	25.3	13.3
Tons N	2.2	3.6

TABLE V.—YIELD TO BE EXPECTED FROM 1,000 TONS OF NEREOCYSTIS.

	Leaf.	Stem.	Total.	Remarks.
Tons wet	775	225	1,000	Counting 3½ times as much leaf as stem.
Dry tons	71	16	86	Leaves average 9.2 per cent dry; stems 7.2.
K_2O tons	12	4	16	Leaves 17.05 per cent K_2O; stems 26.45 per cent K_2O.
N tons	1.54	0.17	1.7	Leaves 2.16 per cent N, stems 1.09 per cent N.

The cost of cutting will be determined by the conditions obtaining at the place of cutting. The results obtained so far indicate that this will be not more than 50 cents per raw ton, and easily may be reduced to 25 cents or less, inclusive of unloading at the dock.

It can not be expected that the cutter now in operation embodies all the perfections to which such a machine is susceptible; nor that improvements in the machine will not reduce the cost of cutting. Certain features of the present method of operation are objectionable. But these almost certainly will disappear when a fuller experience shall have pointed them out and the means of circumventitng them. Cutters of other forms and modifications of the present cutter have been designed and patented. Conspicuous among these are machines ascribed to S. A. Knapp (U. S. P. No. 756,658), and George H. Ennis (U. S. P. No. 1,080,144). In spite of its imperfections the kelp cutter now in operation must be regarded as an unqualified solution of the problem of the economical harvesting of kelp.

The drying of such materials as fish pomace, a class in which kelp likewise may be included, usually is effected in the direct-heat, rotary kiln. It should suffice to say that from *a priori* consideration as well as the results gotten so far in actual experimentation with kelp in the large-sized, hot air dryer and on a semi-commercial scale, this type of dryer seems entirely adapted to the drying of kelp.

Since under Atlantic coast conditions fish pomace and other substances containing 55-60 per cent water may be dried in the direct heat rotary dryer at a cost of about 50 cents per dry ton, it seems reasonable to believe that it should be possible to dry kelp, containing 85-90 per cent water, at a cost of $1 per dry ton.

After drying, it may be found desirable to grind the kelp for mixing. Dry kelp, especially when hot, is quite brittle and grinds easily. It has been estimated that the cost of grinding would be about $1 per ton.

Frye, in his work on Alaskan Kelps, has shown that the leaves of Nereocystis yield 9.2 per cent solid, the stems 7.2 per cent, and that the Macrocystis, stems and leaves together, yield 13.27 per cent solids. Alaria fistulosa produces 13.74 per cent solids. These units were obtained by weighing specimens immediately on being taken from the water while they were still wet with sea water. On the basis of these values and the analyses given in the foregoing tables, the following calculations have been made, showing the yield in various constituents to be expected from a definite weight of freshly cut kelp.

The U. S. Commerce Report states that an effort is being made to develop in the Philippine Islands an industry in the dried juice of the papaya *(Carica papaya)* for medicinal use as a substitute for pepsin. The preparation of this product is represented by the bureau of health officials, who are endeavoring to stimulate its production, as very simple. The fruit is hung above a bowl, and longitudinal cuts are made in the fruit from which the juice drips, hardening soon after falling in the bowl. After being thoroughly dried in the sun it is put in sealed cartons for shipment. Papayas may be grown in almost every part of the islands. The native variety is small compared with the Hawaiian variety which has been introduced and is now grown extensively for the table.

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[12] U. S. Dept. Agri., Bureau of Soils, Circular No. 76.

THE EVAPORATOR AND THE POWER PROBLEM IN ELECTROCHEMICAL PLANTS.*

By OTTO MANTIUS.

The electrolysis of sodium or potassium chloride solutions will produce liquors which with very few exceptions cannot be used or marketed without further concentration. In most cases considerable quantities of water have to be removed, and it is generally acknowledged that the cost for fuel, labor, repairs, interest and depreciation to be charged to the evaporating equipment have considerable influence on the rentability of the whole plant.

During the last few months we have heard a great deal about the conditions under which reciprocating engines, steam turbines or water power can be used for the generation of electric current to best advantage. In this paper I shall present some of the factors and conditions which should be considered when laying out an electrochemical plant where an evaporating system has to work in connection with water power or steam plant.

I shall not attempt to discuss the efficiency of the great variety of cells which are in daily use for the manufacture of caustic liquors, as the figures given below can readily be changed and discounted for any particular system. I shall not go into the question whether water, gas or steam should be used to produce the electric current. I shall restrict myself entirely to the discussion of those features and conditions which have a bearing on the design of the evaporating equipment.

The installation of an evaporator would be a very simple matter if we had to deal with sugar juice, black liquor or packing-house tank water. A double or triple effect for small quantities and a quadruple effect for larger amounts of liquor could be bought, installed and operated at comparatively low first cost and running expenses. The problem of a caustic liquor evaporator is somewhat complicated by the incrustations of the tubes, the corrosive action of the liquor itself and the high boiling point of the more concentrated solution, which practically eliminates the use of a quadruple effect even for large quantities, restricts the operation of a triple effect to certain favorable conditions, and makes a double effect the most economical equipment for a plant of medium capacity.

Inasmuch as this statement is quite contrary to ordinary practice, I give the following figures for steam consumption of various equipments, which will explain and prove my contention:

My calculation has been based on the following assumptions:

Capacity in 24 hours...	20,000 lb. (9,091 kg.) NaOH.
Power required	1,500 E. H. P.
Weak liquor	20,000 gal. (75,750 liters) with 120 grams NaOH and 100 grams NaCl per liter.
Heavy liquor	3,440 gal. (13,200 liters) with 700 grams NaOH and 16 grams NaCl per liter.
Evaporation	16,560 gal. (62,650 liters) in 20 hours = 828 gal. (3,135 liters) per hour.

The hourly steam consumption, including radiation loss, pre-heating of the weak liquor from 70° F. (21° C.) and evaporation of the wash water, will be as follows:

Single Effect—7,900 lb.; 6,000 lb. direct steam, 1,900 lb. exhaust from pumps (3,590; 2,727 and 863 kg.).
Double Effect—5,090 lb.; 3,690 lb. direct steam, 1,400 lb. exhaust from pumps (2,312; 1,676 and 636 kg.).
Triple Effect—4,600 lb.; 3,400 lb. direct steam, 1,200 lb. exhaust from pumps (2,090; 1,544 and 546 kg.).
Triple Effect and Single Effect—4,300 lb.; 3,000 lb. direct steam, 1,300 lb. exhaust from pumps (1,952; 1,362 and 590 kg.).

Single effect and double effect are to be operated with steam at 7 lb. and 20 lb. gauge pressure (0.5 and 1.3 kg. per sq. cm.), triple effect at from 60 lb. to 70 lb. (4 to 4.7 kg. per sq. cm.) and the combination triple effect and single effect with steam at from 7 lb. to 20 lb. (0.5 to 1.3 kg. per sq. cm.). In the latter arrangement the triple effect concentrates the weak liquor to about 400 grams per liter, and the single effect finishes the process to 700 grams NaOH per liter. This arrangement will permit the use of low pressure steam, and should always be used where larger quantities of liquor have to be handled.

The above figures show that the efficiency of the evaporator increases with the number of effects as usual, even if the difference is not as large as might be expected from general practice. The comparatively high steam consumption of the high pressure straight triple effect is due to the increased radiation losses and the large amount of wash waters to be handled and preheating to be done.

These conditions will change as soon as we use a part or all of the exhaust steam of engines or turbines for the evaporation of the caustic liquors.

Where the electricity for the cells has to be generated in a steam plant, either steam turbines or reciprocating engines may be used and the exhaust utilized in the evaporator. As the quantity of steam required for power purposes is about three times larger than the amount needed for the evaporator, the ordinary method of using all the engine exhaust at about 5 lb. (0.3 kg. per sq. cm.) pressure for the concentration of the caustic liquor can only be applied in very small plants by running the evaporator about seven hours per day and operating the engine during the rest of the time in connection with the condenser attached to the evaporator.

In most cases it is necessary to run a multiple effect evaporator continuously and utilize only a part of the steam, which has entered the engine or turbine at high pressure and is withdrawn at from 20 lb. to 30 lb. (1.3 to 2.0 kg. per sq. cm.). I find that for this kind of work steam turbines are not quite as suitable as reciprocating compound engines, as in a steam turbine a large part of the work is done during the low pressure period. While actual tests on small compound engines show that 10 lb. (4.5 kg.) steam withdrawn from the receiver at 20 lb. (9.1 kg. per sq. cm.) pressure require only from 5 lb. to 6 lb. (2.25 to 2.75 kg.) extra steam at 125 lb. (8.3 kg. per sq. cm.) pressure, the guarantees given for large steam turbines ask for 8 lb. (3.6 kg.) extra steam at 150 lb. (10 kg. per sq. cm.) pressure added for 10 lb. (4.5 kg.) steam withdrawn at 20 lb. (1.3 kg. per sq. cm.) pressure.

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*Paper presented at the 26th General Meeting of the American Electrochemical Society, at Niagara Falls, Oct. 1-3, 1914.

To produce 20,000 lb. (9,091 kg.) NaOH in 24 hours the steam plant should develop 1,500 E.H.P. per hour. A compound condensing Corliss engine will use 15 lb. (6.8 kg.) steam per E.H.P. per hour and increase its steam consumption 1 lb. (0.45 kg.) for every 2 lb. (0.91 kg.) discharged from the receiver at 20 lb. (9.1 kg.) pressure or higher.

Assuming that 1 ton of coal furnishes 15,000 lb. (6,820 kg.) of dry steam at a cost of $3.00, *i. e.*, 1,000 lb. (454 kg.) of steam for $0.20, the steam and coal consumption of engine and evaporator combined will then be as follows:

SINGLE EFFECT.

Engine	.....1,500 × 15 × 24 =	540,000 lb.	(245,300 kg.)	steam
Evaporator	......3,000 × 20 =	60,000 lb.	(27,270 kg.)	steam
Pumps	..........1,900 × 20 =	38,000 lb.	(17,270 kg.)	steam
		638,000 lb.	(289,840 kg.)	steam

Fuel cost per day = $127.60; per 1,000 lb. (454 kg.) NaOH = $6.38.

DOUBLE EFFECT.

Engine	.....1,500 × 15 × 24 =	540,000 lb.	(245,300 kg.)	steam
Evaporator	......1,845 × 20 =	36,900 lb.	(16,760 kg.)	steam
Pumps	..........1,400 × 20 =	28,000 lb.	(13,330 kg.)	steam
		604,900 lb.	(275,390 kg.)	steam

Fuel cost per day = $120.98; per 1,000 lb. (454 kg.) NaOH = $6.05.

TRIPLE EFFECT AND SINGLE EFFECT.

Engine	.....1,500 × 15 × 24 =	540,000 lb.	(245,300 kg.)	steam
Evaporator	......1,500 × 20 =	30,000 lb.	(13,635 kg.)	steam
Pumps	..........1,300 × 20 =	26,000 lb.	(11,820 kg.)	steam
		596,000 lb.	(270,755 kg.)	steam

Fuel cost per day = $119.20; per 1,000 lb. (454 kg.) NaOH = $5.96.

A straight triple effect naturally can not be operated on steam of 20 lb. (1.3 kg. per sq. cm.) pressure, and live steam has to be used altogether.

TRIPLE EFFECT.

Engine	.....1,500 × 15 × 24 =	540,000 lb.	(245,300 kg.)	steam
Evaporator	......3,400 × 20 =	68,000 lb.	(30,900 kg.)	steam
Pumps	..........1,200 × 20 =	24,000 lb.	(10,900 kg.)	steam
		632,000 lb.	(287,100 kg.)	steam

Fuel cost per day = $126.40; per 1,000 lb. (454 kg.) NaOH = $6.32.

In all cases evaporators and pumps work only 20 hours per day, while the cells are naturally operated during the full 24 hours.

These figures show that for a production of 3,600 tons caustic per year the cost of fuel is about $2,000.00 higher for a straight triple effect than for a double effect or combination triple and single effect. Besides, we must not forget that a high pressure triple effect is considerably more expensive in first cost and repairs, and is sometimes difficult and even dangerous to operate. Wherever possible, evaporators for caustic liquors of high density should be operated under vacuum, as it will prevent loss of caustic and reduce the corrosive action of the liquor.

Quite a number of electrochemical plants obtain the necessary power at very low rates from central power plants, but have to install boilers to furnish steam for the evaporators. At first glance it would appear that a high pressure triple effect might be the most economical equipment, but the following figures will prove that as far as cost of power is concerned a different arrangement is preferable. Let us assume that only $22.00 is charged for one E.H.P. per year and that 1,000 lb. (454 kg.) steam cost $0.20 as before.

STRAIGHT TRIPLE EFFECT.

Cost of power	.... $\frac{1,500 \times 22}{365}$ =	$ 90.40
Evaporator and pumps	.....4,600 × 20 = 92,000 lb. =	18.40
		$108.80

Therefore 1,000 lb. (454 kg.) NaOH = $5.44.

We have seen before that a combination triple and single effect can be operated at low pressure and uses less steam than a straight triple effect. We can therefore first use the high pressure steam in a special compound engine to furnish a certain amount of power at not any cost for fuel, and then utilize the exhaust for the evaporation of the liquor. Assuming that the engine will use 23 lb. (10.5 kg.) per E.H.P., and therefore produce 130 E.H.P. from the available 3,000 lb. (1,364 kg.), we have only to purchase 1,370 E.H.P. outside power, and the cost will be as follows:

COMBINATION TRIPLE AND SINGLE EFFECT.

Power	.... $\frac{1,370 \times 22}{365}$ =	$ 82.60
Engine and evaporator	.....130 × 23 × 24 = 72,000 =	14.40
Pumps	........................1,300 × 20 = 26,000 =	5.20
		$102.20

1,000 lbs. (454 kg.) NaOH = $5.11.

This would mean a saving of over $2,400 per year, less interest, depreciation and repairs of engine. Quite frequently it might not be desirable to install such an engine, but there will always be a number of pumps and small engines the exhaust of which should be used in the evaporating equipment.

We could even go a step further and install a 500 E.H.P. compound condensing engine, use in the evaporator steam taken from the receiver and contract for only 1,000 E.H.P. to be taken from the central station. Considering the cost of extra labor, repairs and depreciation, we would not save much, but the engine could be arranged so as to take up the peak load, for which otherwise in most cases heavy penalties have to be paid, and the plant could be operated at two-thirds of its normal capacity by shutting down the engine without having to pay for more than the 1,000 E.H.P. Besides, the plant has not to be closed down entirely in case the central plant should not be able to furnish the current.

Similar conditions prevail in plants where gas engines or heavy oil engines are used to generate the current for the cells. A double effect or combination triple and single effect using exhaust steam from auxiliary engines and pumps will give the best results.

A type of engine used very little in this country is the Lentz patented superheated steam engine, which even in small units will produce current at surprisingly low cost. I was told last year during a visit to Germany that one E.H.P. can be produced by 10 lb. (4.5 kg.) of steam and less in a 300 kw. unit. This would make the Lentz engine the ideal motive power for small plants furnishing bleach liquor and caustic for paper mills.

The foregoing figures lead to the conclusion that a straight triple effect operated with high pressure steam should never be used for the concentration of caustic liquors. The first cost is high, and the expenses for fuel, repairs and renewal are more than for any other arrangement. Besides, such a triple effect is considered by many people a general nuisance and source of trouble on account of the difficulties in keeping joints and valves tight.

As far as the cost of fuel per 1,000 lb. (454 kg.) $NaOH$ is concerned, there is not much difference between a single, double or combination triple and single effect, but low first cost and simplicity of operation should induce us to choose a single or double effect for small capacities up to 5 tons $NaOH$ per day; for larger plants, and especially where the cost of coal is high, and large amounts of cooling water can be had at only considerable expense, a double effect or combination triple and single effect should be installed. The proper arrangement has to be determined for each plant, and no general rules can be given.

I wish to add a few words concerning the general design of the evaporating equipment:

1. For small single effects operating only ten hours per day no reserve is needed, as all repairs can be done over night. The piping of multiple effects running continually should always be arranged so that any pan can be cut off entirely for repairs.

2. Steel, charcoal iron or nickel steel tubes should be used only up to 40° Bé., as the corrosive action of caustic up to this density is very small, and any kind of tube will last a long time, unless the liquor contains a considerable amount of corrosive impurities.

3. For the concentration from 40° to 50° Bé. and higher, only special cast iron tubes should be used, because cast iron is the only material that will withstand the action of the hot concentrated caustic liquor. In Germany almost all the caustic liquor above 40° Bé. is handled in cast iron evaporators. The first cost of such an equipment is somewhat higher, but this difference is soon paid for by the saving in repairs and the increased efficiency of the plant, as there is no time lost in shutting down to replace worn-out tubes. Some of the largest manufacturers of caustic prefer to use copper tubes almost exclusively, as copper will wear longer and more uniform than steel or charcoal iron. Besides, the scrap value of the discarded tubes is quite high. On the other hand, the first cost is considerable, and where large amounts of salt have to be handled the copper tube disappears quickly on account of the mechanical abrasion caused by the salt passing along the copper surface at high speed.

It was not my intention to consider all possible combinations between evaporator and the source of power, as this is not the time and the place to make such an exhaustive investigation. I only wished to point out the economic and practical disadvantage of a high pressure straight triple effect when handling caustic liquor up to 50° Bé., and the good results that may be obtained from a compound or triplex condensing engine when working in connection with a double effect evaporator or a combination of low pressure triple effect and single effect with a cast iron heating surface.

NOTES ON SIZING PAPER WITH GELATIN.*

By F. CYSTER.

In the investigation of the many complaints addressed by the customer to the seller with reference to the quality of paper with which he is being supplied, it is occasionally found that the papermaker is at fault. On these rare occasions the trouble may usually be traced to anxiety on his part to preserve the high standard he has previously created.

A case in point was furnished some time ago by the complaint of a customer with reference to a paper the furnish of which was a mixture of bleached sulphite wood and rag, chiefly cottons. The complaint was to the effect that the paper did not handle so well, and that the customary firmness and "rattle" were lacking. An analysis of the paper showed that the making in question contained rather more than the usual amount of cottons, and although the sheet was "prettier" and superior in other respects to the usual thing, the customer's wishes would have been better met by closer adherence to the former and cheaper composition.

Another complaint, which with some of a kindred nature suggested the following notes, was with reference to an animal-sized memorandum paper from which typewritten letters were duplicated, using a previously damped cloth as a vehicle for the moisture. The complaint was that after being in use a short time the cloth became clogged and partly sized in such a way as to interfere with the even distribution of moisture, and therefore also with the duplication of type.

The fault in this case was a larger amount of gelatin than in the paper which gave satisfactory results, and some of the excess was conveyed during contact to the cloth. It is not unusual also, with some high class tub-sized papers, to find the gelatin applied in such a way as to create difficulty when writing in the ordinary way with ink, and the pen will occasionally persist in repeating in miniature the antics of an inexperienced dancer on a highly polished floor.

Facts like the foregoing with regard to gelatin suggest that there are limits to the quantity essential to produce the best all-round results. The tub-sizing process is primarily intended to produce a continuous surface sizing of ink-resistant gelatin, and it is easier to exceed than to regulate the amount necessary to perform this, imparting at the same time the attractive writing surface.

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*From the World's Paper Trade Review.

The amount of gelatin absorbed into the body of the paper will vary largely with different classes of paper, being controlled by considerations such as finish, closeness of texture and capillarity of the paper on the one hand, and the temperature and consistence of the size on the other.

The gain in strength which always accompanies gelatin sizing (by which is meant the passage of the web through the bath *after* the paper machine and subsequent slow natural drying) is the natural effect of the better cohesion of the sized fibers. The degree of added strength produced in this way, however, is of course limited by the amount of gelatin which can be applied subject to the previously mentioned considerations, and no amount of gelatin sizing can replace the peculiar qualities with regard to the strength and endurance acquired by the sheet through the judicious selection of the raw material and its subsequent skilled treatment in the beater and on the machine.

This applies also to the added resistance to deterioration by general wear and tear, closely related to tensile strength, which is characteristic of the tub-sized paper, as here again the question of "length of life" of the paper depends largely on the same conditions which govern the strength. The term "durability," however, is capable of application in another direction, i. e., that of resistance to chemical action, and it is necessary to differentiate the meaning of the term when used in this connection from that which is implied by the measure of its resistance to folding and friction.

It is quite possible that two papers made in the same way as regards beating and treatment at the machine, and from the same raw material, may give the same results when tested for strength and resistance to friction directly after manufacture, and yet to behave quite differently when stored for a length of time, supposing that one of the papers contains a quantity of injurious compounds which should have been removed before manufacture.

In this connection the application of gelatin can hardly improve the durability of paper when viewed in its capacity to withstand chemical action, either inherent or communicated, since pure cellulose, as exemplified by the cotton fiber, is less liable to deterioration than gelatin. It is one of the most stable organic compounds known, and is capable of resisting to a remarkable extent the action of strong chemicals. Gelatin does not deteriorate readily in the dry state, but this cannot be said of it under conditions of abnormal dampness, when it is liable to the development of fungi and consequent decomposition.

The addition of alum or sulphate of alumina is the usual practice in preparing the gelatin bath, and its thickening action on the solution is well known. Alum causes the gelatin to form on the surface of paper a more difficultly soluble and water-resisting skin. It lessens the penetrative power of the size, keeping it on the surface, and gives the paper a firmer effect than if the gelatin is allowed to keep its original more fluid condition. The excessive thickening of the size with alum has, however, attendant dangers, i. e., the surface skin may be made so insoluble that a pen glides over the paper without leaving any ink impression, and also the dried paper may show innumerable glistening points, not unlike the mica particles shown in the finished sheet by using badly levigated kaolin.

In the following comparison of trials made with gelatin only, and with gelatin with the addition of alum, although in the former case the total absorption was higher, the peculiar phenomena mentioned were absent, which was by no means the case in the papers treated with alum gelatin. In connection with the surface difficulty it must also be remembered that the consistence, or more correctly perhaps the fluidity, of the size solution and its penetrative power are largely questions of temperature, and paper sized in a bath in which the heat is not sufficient to preservee perfect fluidity is bound to be unsatisfactory.

As already indicated, the penetration of the sizing solution is controlled by other considerations than those of temperature and fluidity of the size, the degree of engine sizing being perhaps the most potent factor. Paper sized mechanically by passing the web through a trough of gelatin solution is subjected to the longitudinal tension necessary to steadily unwind the reel into the bath. If the paper be unsized the hot solution with which it comes into contact is immediately absorbed through the section, and the resulting softening often causes the web to become so weak as to be unable to withstand the tension. Partial sizing in the beater is resorted to, and the ultimate absorption of gelatin consequently lessened. Hand-made paper, or machine-made cut into sheets and sized by hand, has only, of course, to support its own wet weight, and can therefore be wholly gelatin sized. In this way the heavy gelatin content of the hand-sized product is of great assistance in imparting the distinctive character which such papers possess.

In order to make a direct test of the absorbent qualities to gelatin solution of papers sized to different degrees with rosin, trials were made with papers sized in successive stages with 0.5 per cent of rosin, calculated on the air-dry weight of the sheet. The composition chosen was well beaten rag with no addition of any kind. Sheets were made by hand to a substance of 120 gm. per square meter, first with the waterleaf stuff, and then from the pulp sized in the stages indicated above to 2½ per cent. The regularity of the substance of the sheets was maintained by constant additions of stuff equal to the quantities removed. The air-dry sheets were afterwards sized by immersion for twenty seconds in a 5 per cent solution of gelatin, to which was added 8 per cent of sulphate of alumina on the weight of gelatin, corresponding to the formula $Al_2 3(SO_4).12H_2O$. The excess of gelatin was removed in each case by rubber-covered rolls under a constant pressure. The results are set out in Table I:

TABLE I.

Sheet.	0	1	2	3	4	5
Percent rosin size	0.0	0.5	1.0	1.5	2.0	2.5
Percent gelatin absorbed on original dry weight of sheet	10.2	9.1	7.5	6.5	5.7	5.2

The comparative small difference made by addition of the first 0.5 per cent rosin size to that of the second is probably accounted for by the fact that its efficiency would be lessened owing to the hard water present. The most marked difference is made by the addition of 1 per cent, the consecutive additions having regular but smaller effect. It will be seen that the sheets sized with 2½ per cent absorb approximately only half the quantity shown by the completely waterleaf paper.

Table II illustrates the greater fluidity and penetrative power of gelatin prepared without alum, but using as a preservative a small amount of formaldehyde. Duplicate tests to the above were made, the gelatin solution being of the same strength but prepared without the addition of aluminum sulphate.

TABLE II.

Sheet.	0	1	2	3	4	5
Percent rosin size	0.0	0.5	1.0	1.5	2.0	2.5
Percent gelatin absorbed on original dry weight of sheet	12.1	10.9	8.9	8.0	7.2	6.5

These sheets had the advantage of being completely free from the glistening minute scale mentioned earlier, but lacking in the crisp firmness of the other samples. The ink-resisting qualities also were not so good.

The above results are not given as constant, definite proportions of gelatin absorbed under all conditions by papers containing the quantities of rosin mentioned. The figures would be modified by many considerations. But whatever the quantities of gelatin ultimately held by the sheet, the differences between papers rosin sized as above should bear a corresponding relationship.

With regard to the finished sizing efficiency of the papers used in the experiments, this was not estimated with the exhaustiveness necessary to give the tests comparative numerical expression, but the advantage was with the sheets containing the greater amounts of gelatin, although the degrees were not so marked as the differences of gelatin content would lead me to suppose, and could not be distinguished by ordinary ink writing.

The process of tub-sizing, in common with other important operations in connection with paper manufacture, is to the casual observer a simple operation, containing little more than is obvious, the chief difficulties seeming those of manipulative skill. It will be seen, however, that the best results depend on the consideration of the subject in all its aspects, both from the point of view of the paper and the size, and in their application with a view to suiting the finished article to the particular purpose for which it is intended.

NITROGENOUS FERTILIZERS FROM REFUSE SUBSTANCES.*

By CARL ELSCHNER.†

A large quantity of organic refuse and waste substances is obtained from the wool and shoddy manufacturing, rag sorting, felt manufacturing and dehairing of hides in tanneries and slaughter houses. These form a splendid material for the manufacture of high-grade dissolved nitrogenous fertilizers. These articles are by no means to be ranked with wool-meal and leather-meal, both of which show a very slow effect as plant foods.

Sometimes it has been recommended to carry these crude materials, such as wool-waste, felt and leather clippings, old shoes, wooden rags, old felt articles, hair, skins, etc., on the field and bury them in the ground. In the course of time a part of the nitrogenous matter would be taken up, as such substances would slowly decompose, but much, if not the greater, part of the nitrogen will be lost. Hair and wool, even when converted into a very fine powder, decay very slowly and after a number of years the unchanged substances can be found in the soil.

Raw hide would decompose in comparatively little time. However, if it is converted by the use of tanning material into leather, the tannic acids have pronounced antiseptic properties and act as a preservative on the material. This of course is a great disadvantage to the decomposition. For intsance, it takes many years before an old leather boot will disappear by decay and be converted into a substance available as plant food. It has therefore been proposed either to destroy the tannic acids in the leather or to dissolve the raw material in acids or other chemicals. The most simple process now in use is, to roast the leather refuse in a furnace or a kind of strongly heated dryer, after a little sulphuric acid has been sprinkled over it. This roasted leather can easily be ground, but there is quite a loss of nitrogen. By the roasting of the leather, the tannic acids are partly destroyed and so the fertilizing value of the leather-meal is considerably higher than that of the untreated leather; but even then the fertilizing effect is very slow compared with other nitrogenous substances such as nitrates or sulphate of ammonia, and only when the price of such leather meal is low would the application of it be profitable.

To incorporate nitrogenous organic matter with superphosphates derived from raw phosphate rock and degelatinized bone-meal, it has been proposed by many factories to mix ground leather, hoof and horn-meal, also cottonseed meal with ground phosphate rock and sulphuric acid to make an ammoniated superphosphate. The different nitrogenous substances vary much in their contents. For instance, shoddy contains from 3 to 12 per cent ammonia; pure wool and hair from 13 to 17 per cent; chrome leather about 8 to 11 per cent; leather clippings and shavings from 6½ to 10 per cent; felt clippings from 9 to 16 per cent; old shoes, which are often unprofitable to work on account of the nails, from 4½ to 8 per cent; old felt slippers as they are picked out by the junk dealers from 8 to 12 per cent.

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*From The American Fertilizer.

†Consulting Chemical Engineer, San Francisco, Cal.

I have succeeded in mixing the comparatively cheap sheared wool from carpet and rug factories—with about 13 per cent ammonia—directly into the degelatinized bone meal and acid mixture, with an addition of carbonate of lime or better dolomite. The latter keeps the mixture liquid for a longer time, and I have obtained products containing 3½ per cent of ammonia and 12½ to 14½ per cent water soluble phosphoric acid. The usual method is to place the refuse in a tank with slightly heated sulphuric acid of 50° to 60° Bé. If nitric acid is present it is more favorable. The refuse finally dissolves in the acid which can then be utilized for dissolving raw phosphate or bone-meal. It is practically necessary on account of the adhering gluish condition of the ammoniated superphosphate thus obtained to use artificial drying; a final content of 2½ to 3½ per cent ammonia in such fertilizer is considered a very high percentage.

To produce fertilizers with a higher content of ammonia, in order to obtain a product of high quality, it is necessary to dissolve the refuse substance and then dry the product either by means of a chemical process or by the application of heat. In this way one firm in Germany heats the refuse with sulphuric acid and saltpeter, whereby the mass can be more quickly dissolved than with sulphuric acid alone. The liquid is then mixed, after a further evaporation, with sulphate of ammonium and a drying body such as peat. It is understood that there is a slight loss of the nitrate nitrogen. Through the application of 5 kg. nitrate on 100 kg. refuse, the process may be described as an incomplete Kjeldahl process, such as is used in the chemical analysis of organic nitrogen.

The two processes of von Krottnaurer are scientifically very interesting. According to these processes, which produce the same kind of fertilizer but employ different machinery, the refuse is dissolved in diluted sulphuric acid—leather refuse, under some circumstances in over-heated water without acid—under pressure at a temperature of 120° to 150° C. and then dried. A newer process uses a continuous working steam apparatus, which consists of a double hollow cylinder, with specified heating tubes, a funnel, and below, a suitably, easily heated hollow cylinder. The latter is so placed that between it and the boiler there is a narrow intermediate space, out of which the mass runs, which is then dried.

One can divide this process into two phases—the dissolving under pressure, and the drying. After the action of the diluted, heated sulphuric acid upon the refuse for one-half to two hours a dissloving takes place; if the acid is concentrated too far, a formation of a carbon substance occurs. The product is too a great extent amido-acetic acid (glycocoll), which is in solution. During the process of drying the liquid the amido-acetic acid (or glycocoll) separates into leucine and similar bodies (tyrosine, etc.), and the decomposition continues in part as far as to ammonia. In strongly decomposed raw material, some cyanformicic acid also occurs. An average product of such nitrogenous, dissolved material contains 8½ to 9 per cent ammonia, or, with the addition of bone-meal, a fertilizer of 7½ per cent ammonia besides the phosphoric acid.

The drying takes place on the surface of heated cylinders, which are slowly revolved in such a way that they dip, to about one-fourth of their diameter, in the syrup of the dissolved refuse substance, which, by its sticky, glue-like properties adheres to the cylinder and dries on it in the form of a crust. The more leather it contains the more thick and sticky the solution is. This dried crust is removed from the cylinder by a system of scrapers or knives.

In order to use less steam for drying I modified this process in such a way that the refuse substances, which should always contain some leather, are put in a revolving drum of a certain form, which is heated by direct fire, with a certain addition of sulphuric acid. Leather alone needs only about 5 per cent of its weight of sulphuric acid, and a little water should be added if the refuse is too dry; while felt and hair require 20 to 30 per cent of their weight of acid. A few handfuls of nitrate of soda causes a stronger dissolving effect. Then the drum is revolved, and after heating for one-half to two hours the contents become a putty-like mass, which when cooled off becomes hard and brittle.

On account of the surplus of acid it is necessary to add either some ground phosphate or bonemeal, which removes the acid and converts the phosphate into an available state, or some burnt limestone powder may be added. The drum must, after that addition, revolve a few more times, and then the hot, black mass is taken out to cool; after grinding it forms a brown powder. It is absolutely necessary that the raw material does not contain more than 20 to 25 per cent moisture, as otherwise the dissolving of the substances takes a long time. The odor of the manufacturing is not specially disagreeable, being like burnt chickory, but is of course disliked by the neighborhood when it is constantly present. For this reason the vapors ought to be carried into a smoke stack and at the same time some ammonia be introduced into the fumes, which will successfully neutralize the odorous, escaping vapors.

Among the processes used extensively in European factories one may be mentioned on which the patent has expired. This process of producing fertilizer containing ammonia out of refuse containing nitrogen utilizes a dry, mild heating of the refuse saturated with dilute sulphuric acid in two heating periods. At first through heating to 100° a concentration of the sulphuric acid in the substance is secured and afterwards through a further heating up to 250°, a complete drying and destruction of the fiber of the refuse is produced. This is done in such a way that a combustion cannot take place in consequence of the low temperature and the presence of the sulphuric acid.

CAUSES OF DEFECTS IN SULPHITE CELLULOSE.*

By R. R. OLIVER, F. C. S.

When wood is boiled in a solution of calcium bisulphite under pressure the incrusted substances are broken down and the resulting mass when washed yields a pulp suitable for the manufacture of paper. While this sounds simple enough, various complications develop at times, and these often start with the preliminary treatment of the wood and extend into the actual boiling. If not carefully watched and provided against, the complications referred to will lead to trouble that will become apparent in the production of an inferior grade of sulphite paper.

When black specks make their appearance in the pulp, it may be taken as an indication that the bark has not been completely removed, though the specks may consist of foreign substances such as particles of rubber, belt lacing or leather which have found their way into the digester.

Failure to remove all of the bast from the wood often leads to the appearance of brown fiber bundles. Brown particles also make their appearance when portions of the wood have become overheated in the boiling, but these disappear on bleaching.

Unevenness of chips leads to the occurrence of large brown bundles of fiber that come out in practically the same shape and firmness as when they went in. By proper adjustment of the slits in the splinter-catcher these bundles can be kept back.

When the cellulose as it comes out of the digester has a brownish or yellowish color instead of a good white appearance, it is an indication that an insufficient amount of bisulphite was present toward the end of the boil.

When the wood at the end of the cook remains brown and hard it is an indication that the solution contained polythionic acid, the result of improper preparation of the liquor. The action of this acid is to deposit calcium sulphate and sulphur on the wood. These are insoluble substances which are formed at the expense of the acid liquor.

Microchemical Tests.—When an insufficient quantity of water has been used in the boiling, small earthy particles of neutral calcium sulphite can be seen distributed among the fiber when the latter is examined under the microscope.

A microchemical test may be carried out in a satisfactory manner by using a low-power objective and a slide having a concave center. A microscopic sample of the moist pulp is introduced on the side, a drop of distilled water added and the pulp teased out and examined with the microscope adjusted for the best possible detail, using an Abby condenser and shutting off most of the light.

When the particles having an earthy appearance are detected, a few drops of a 5 percent solution of hydrochloric acid are added, which dissolve the neutral calcium sulphate of which the particles consist. From this it might be thought that it would only be necessary to add a little hydrochloric acid to the wash water in order to overcome the condition, but sulphite pulp so treated would require an excess of bleach to obtain a good white.

When a pure white sulphite cellulose changes to a yellow or grayish color during the washing process it may be taken as an indication that iron is present, the source of contamination being usually the wash water.

To test for ferruginous impurities, evaporate some of the water in a clean white porcelain dish. If a reddish brown deposit is produced it must be carefully collected and dissolved in a little hydrochloric acid and this should be completely oxidized by heating with an addition of a little potassium chlorate. Dilute the solution, cool and add a few drops of a 10 percent solution of potassium ferrocyanide, when, if iron is present, a blue precipitate will be formed.

The council of the International Association for Rubber Cultivation in the Netherlands East Indies offers an international competition for (1) a plan for a complete rubber estate factory principally for making "crepe," and (2) a plan for a complete rubber estate factory principally for making "smoked sheet." Both plans are to be drawn in such a way that at first the capacity of the factory will amount to 100,000 kilos (220,460 pounds) of dry rubber per annum, which by three extensions can be increased to 250,000 kilos (551,156 pounds). The projects should be accompanied by a detailed description of the factory and of the way in which the competitor considers the product should be treated, and also of the necessary machinery. Projects may be made in English, and should be sent in before March 1, 1916, either to the office of the association, 13, Kneuterdyk, The Hague, Netherlands, or to the office of the "Algemeene Vereeniging van Rubberplanters ter Oostkust van Sumatra" at Medan (Deli), Dutch East Indies. For the best project a prize of 1,500 florins ($603) is offered, and a prize of 500 florins ($201) will be given for the second best project.

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*From Paper.

THE UTILITY OF SULPHUROUS ACID AND PURE YEAST IN CIDER VINEGAR MANUFACTURE.*

By W. V. CRUESS, J. R. ZORN and A. V. SIFREDI.

A study of methods of alcoholic fermentation of apple juice destined to be made into vinegar in various California factories showed that in almost every case no attempt was made to control the micro-organisms of fermentation. A brief description of the various ways of handling the cider stock will no doubt be of interest.

In one of the largest factories the cull apples and peels and cores from apple driers are ground or "grated" in an Ohio apple grater as soon as received. The juice is pressed out with heavy screw presses driven by a motor and cog gearing with a capacity of 60 tons per day. The juice goes to 20,000 gallon tanks. The first tank of the season is started with a large starter of compressed yeast. When this tank is in fermentation, about one-third of its contents is used to start the next tank. The third tank is started from the second, and so on through the whole series of tanks. Over 500,000 gallons are made in this way during a season. Examination of the fermented juice showed it to be "dry"; that is, practically free from unfermented sugar, but it was shown by microscopical examination to contain large numbers of lactic acid bacteria and the large tanks soon developed a heavy growth of *mycoderma* (wine flowers) after alcoholic fermentation. The lactic bacteria develop a "mousey" flavor and the mycoderma rapidly oxidizes alcohol to CO_2 and H_2O without forming any corresponding amount of acetic acid.[1] Laboratory tests demonstrated that mycoderma isolated from cider was capable of destroying all of the alcohol of a fermented orange juice containing 4.5 per cent alcohol in three weeks. The gravity of heavy mycoderma growth may be seen from these figures.

Another large factory stores its cull apples, peels and cores in a large wooden bin. Often this material undergoes a fermentation, resembling silage fermentation, before it can be crushed. The juice after crushing and pressing is allowed to undergo spontaneous fermentation in 30,000-gallon tanks. Wild yeasts, lactic bacteria and mycoderma develop profusely, giving a very cloudy cider. Occasionally a tank "sticks" with some unfermented sugar, but in general the fermentations are complete.

A third factory (until 1914) crushed its apples and allowed the crushed apples to undergo spontaneous fermentation 3 or 4 days before pressing. This method gave a high yield of juice, due to the softening effect of the fermentation. Beginning with this season, this factory used pure "Burgundy" wine yeast on the crushed apples with good results. The yeast was propagated according to Bulletin 230 of the University of California Experiment Station. No sulphurous acid is used on the crushed apples, consequently the fermented cider shows a strong tendency to develop mycoderma.

The above factories all use the generator process for converting the alcohol to acetic acid. A fourth factory making 50,000 to 75,000 gallons per year uses the slow process throughout. Fermentation is allowed to take place spontaneously with the result that lactic acid bacteria, as well as mycoderma, grow vigorously in the fermented cider. There are also a few fermentations that "stick," *i. e.,* stop before the sugar is completely transformed to alcohol.

On account of these obvious defects in present methods, the experiments described below were carried out to see if the beneficial effects of pure yeast and sulphurous acid obtained with wine fermentation in 1911[2] could be duplicated with apple juice fermentation.

SMALL SCALE FERMENTATIONS.

Two barrels of the same juice were taken. Barrel "A" was allowed to ferment naturally; barrel "B" was treated with potassium metabisulphite ($K_2S_2O_5$) at the rate of 12 oz. per 200 gallons or approximately 175 mg. SO_2 per liter. It was allowed to stand 24 hours; was then drawn off into another barrel and pure "Burgundy" wine yeast was added. A summary of the two fermentations appears in Table I and may be stated as follows:

1—Increase of 1.8 per cent alcohol.

2—More complete fermentation of sugar.

3—Elimination of wild yeasts and lactic bacteria; probably due to action of SO_2 during first 24 hours.

4—More rapid clearing of the cider and the vinegar.

5—Improved and cleaner flavor.

6—More rapid acetification after alcoholic fermentation.

30,000-GALLON FERMENTATIONS.

A 30,000-gallon tank (No. 10—Table II) of apple juice was filled with juice from culls, peels and cores during a pressing period of three days. Samples were taken during filling and analyzed for Balling degree, alcohol and total acid. The juice was allowed to ferment spontaneously and was handled by methods ordinarily used in this factory.

A similar 30,000-gallon tank (No. 16) was filled with similar juice. Before going to the large tank, each 1,000 gallons as it came from the press was held temporarily in a 1,000-gallon vat and treated with 8 oz. metabisulphite per 200 gallons. This was added from a solution of 8 oz. metabisulphite per gallon in water. The first 2,000 gallons to go into the large tank were started with 100 gallons pure "Burgundy" yeast and left till next morning before any more juice was added. It took three days to fill the 30,000-gallon tank. By the time the tank was full in each case, fermentation had progressed so far that no attempt at a fermentation record was made. Table II shows the effects due to the sulphurous acid and pure yeast: gain due to pure yeast and SO_2 was found by subtracting 15.20 from 16.27 to give difference in sugar = 1.07 per cent. This was divided by 1.7 to get its alcohol volume per cent equivalent as it is considered that 1.7 per cent sugar gives 1 per cent alcohol in practice. This figure, 0.73 per cent, subtracted from 2.05 gives 1.32, the "net increase" in alcohol due to pure yeast.

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*From The Journal of Industrial and Engineering Chemistry.

[1] A. V. Sifredi, Thesis for M. S., Univ. Calif., Dec., 1914.

[2] F. T. Bioletti and W. V. Cruess, University of California Expt. Sta., Bull. 230.

TABLE I.—RESULTS OF EXPERIMENTS WITH SULPHUROUS ACID AND PURE YEAST IN BARREL TESTS.

Fermentation Record, Barrel A.
(Natural Fermentation)

Date.	Balling.	Observations.
Sept. 5	16.0	Filled barrel A
Sept. 8	13.5	Fermenting vigorously
Sept. 13	5.0	Fermenting slowly
Sept. 19	3.0	Fermenting very slowly
Sept. 30	3.0	Strong "mousey" flavor: many lactic bacteria
Oct. 13	3.0	
Jan. 9	0.0	Still tastes sweet

Fermentation Record, Barrel B.
(Pure Yeast and SO_2)

Date.	Balling.	Observations.
Sept. 5	16	Filled barrel B and added SO_2
Sept. 6	16	Racked into another barrel and added 2 per cent by volume of pure Burgundy yeast
Sept 8	14	Fermenting vigorously; taste clean; aroma much cleaner than "A"
Sept. 30	1	Fermenting slowly; microscope shows absence of wild yeasts or bacteria of any kind
Jan. 9	0	Taste clean and dry. Much clearer than "A"

Analyses of Barrels A and B.

Sample.	Balling (Brix)	Total Acid as Acetic.	Total Reducing Matter as Sugar	Alcohol per cent by Vol.
Original juice..	16.0	0.60	15.00	0.00
Barrel A Jan. 9	0.0	0.84	0.55	6.20
Barrel B Jan. 9	0.0	0.61	0.037	8.00
Barrel A Apr. 5	...	1.18	0.60	5.60
Barrel B Apr. 5	...	5.90	....	2.56

The results of the large scale fermentation were satisfactory, showing a very material increase in alcohol due to pure yeast and sulphurous acid. Microscopical examination showed that the pure yeast and sulphurous acid gave a much cleaner fermentation than the natural fermentation.

TABLE II.—RESULTS OF 30,000-GALLON TANK TESTS.
Results in Percentages.

	Tank No. 10. Natural fermentation.	Tank No. 16. Pure yeast and SO_2.
Before Fermentation—		
Total solids + (alcohol × 1.7). Average of samples	15.20	16.27
After Fermentation—		
Total acid as acetic	0.568	0.652
Volatile acid as acetic	0.160	0.108
Extract	3.70	3.60
Alcohol: Volume per cent	6.35	8.40
Calculations—		Calculations.
Difference in total solids + (alcohol × 1.7) in tanks 10 and 16		1.07
Alcohol equivalent to difference in total solids		0.73
Difference in alcohol in fermented liquids		2.05
Net gain in alcohol due to pure yeast and SO_2		1.32

SUMMARY.

The use of pure yeast and sulphurous acid in barrel fermentations gave increased yield of alcohol, more complete fermentation of the sugar, a better flavor, more rapid clearing, a fermented liquid practically free from lactic bacteria and *mycoderma vini,* and a more rapid change of alcohol to acetic acid after alcoholic fermentation. This indicates disappearance of practically all of the active sulphur dioxide because acetic bacteria have been shown to be very sensitive to it. Large scale fermentations with pure yeast and sulphurous acid gave an increased yield of alcohol and a cleaner fermentation. Examination of several factories shows the extreme need of some method of control of alcoholic fermentation, and to supply this need the use of small amounts of sulphurous acid to eliminate wild yeast and the addition of pure selected yeast to give a rapid and complete fermentation seems the most practical means of producing the desired results.

AN IRON-BORON-CARBON-COPPER ALLOY.

A patent issued recently to Edward D. Gleason. Brooklyn, N. Y., and assigned to the Neu-Metals & Process Co., Long Island City, N. Y., covers an alloy that is practically non-corrosive and which, though hard and tough, may be rolled to sheet form or readily machined without being annealed. It is an alloy of iron, boron, carbon and copper. The boron is first incorporated in the copper so as to be in excess of the amount that will combine with copper. As the boron associates with iron as readily as silicon, regardless of the carbon content of the iron, the copper is thus caused to alloy with the iron and carbon, forming a homogeneous mixture. By taking 80 parts of Bessemer scrap and fusing it in a furnace and adding 20 parts of copper containing boron in excess, an alloy is produced which may be cast in ordinary sand molds forming castings homogeneous and easily machined.

METALLURGY

THE TESTING OF ORES FOR THE CYANIDE PROCESS.*

By **WELTON J. CROOK.**

AGITATION TESTS.

The extraction of gold and silver from ores by the cyanide process is based on the fact that these metals or their compounds form soluble double cyanides in the presence of free alkalin cyanides. In dissolving gold, the reaction according to Elsner is $4KCN + 2Au + O + H_2O = 2KOH + 2KAu(CN)_2$. Similarly the reaction for the solution of Ag_2S is believed to be $Ag_2S + 4KCN = K_2S + 2KAg(CN)_2$.

In making tests on an ore in order to determine its amenability to cyanide leaching, weighed portions of the ore are agitated in cyanide solution for varying intervals of time and with varying strengths of solution.

The residues are washed free from solution and assayed. The results obtained from these assays are subtracted from the assay of the ore, the difference representing the values removed by the cyanide. Usually no effort is made to recover the values from the solutions when running small laboratory tests, though such a proceedure would furnish an excellent check on the assay of the residue.

ADDITION OF LIME.

The weight of lime to add to each test may be determined by the following formula:

Grams of lime = $0.0005AB$.

When A = weight of ore sample in grams.

B = pounds of lime needed per ton ore.

PREPARATION OF SOLUTION.

It is generally the custom in the laboratory to have a quantity of strong cyanide solution on hand which may be diluted to make solutions of various strengths for the agitation tests. A stock solution containing at the rate of 40 lbs. KCN per ton (2%) has been found convenient.

When preparing the leaching solutions, the strength of the stock solution is first determined and the following formula made use of:

$$\frac{Q \times \% W}{\% S} = \text{cc. strong solution}$$

And Q — cc. strong solution = cc. water to add

When Q = cc. of weak solution wanted

W = weak solution

S = strong solution.

When making mental calculations of this character, it is very useful to remember that 1 lb. per ton is equivalent to 0.05%. For example, if a tank contained 500 lbs. of solution which tested 0.05% KCN and it was required to raise the strength to 0.10% KCN by the addition of solid cyanide, then each pound added per ton gives an increase of 0.05%. The increment required is 0.05%, so that for one ton of solution 1 lb. of solid KCN must be added and for 500 lbs. of solution ¼ lb. would have to be added.

When a weak solution is to be built up by the addition of a stronger solution, the strength of each being known:

$$X = \frac{A(a-c)}{b-c}$$

And A — x = cc. of strong solution to add

When A = cc. of solution desired

a = % KCN in solution desired

x = cc. of weak solution in mixture

b = % KCN in weak solution

c = % KCN in the strong solution.

Unless the per cent KCN in the strong solution is determined very accurately and the portions of water and strong solution measured out very carefully, results of only approximate correctness can be expected. All prepared solutions should be carefully checked by titration with silver nitrate.

GRINDING THE ORE.

The average mesh to which ore is now crushed for cyanide treatment is probably 100 mesh, and this is taken as a convenient starting point.

About 1½ kilograms of the ore to be tested (10 mesh) are weighed out and screened through a 100 mesh screen and the oversize is crushed in a gyratory or disc laboratory crusher and ground to pass this mesh.

In regard to the grinding, it should be borne in mind that in making tests care should be taken that the results reported are obtained on ore of the same mesh as stated in the report. Much more favorable results will generally be obtained on 150 mesh material than on 100 mesh. Hence, it would be misleading to report results on 150 mesh material as being obtained on 100 mesh. In practice, fine grinding is expensive and the metallurgist should know exactly the mesh of the ore so that he may balance the cost of grinding against the increased extraction.

The mesh of the ore, as the term is generally used in mill work, gives a clue to the size of the coarsest particles. For example: All the ore in the large sample used in this test (Pahasapa, Vol. IV, No. 2, page 32) was ground to pass a 10 mesh screen. If a sizing test were run on this ore, some material would be retained on a 20 mesh screen and some would pass a

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*From The Pahasapa Quarterly.

200 mesh screen. The proportion of very fine particles to those just passing the limiting screen is a function of many factors, notably, the character of the grinding machine and the friability of the ore.

It is well in starting the fine crushing, to make a trial adjustment of the laboratory disc crusher and run through a small quantity of the ore and if more than one-half goes through the screen, adjust to give a coarser product. Repeat until satisfactory results are obtained, then run through the entire sample. Regrind the oversize, adjusting the machine to give a slightly finer product. In all, four or five regrindings are required to give a product not too fine.

After pulverizing, mix the ore thoroughly on a rubber cloth, then spread out in a thin layer and take dips with a spatula from various parts of the layer for each portion weighed.

THE AGITATION.

Place 100 grams of ore in each agitation bottle and add the required amount of lime (Pahasapa, Vol. IV, No. 1, p. 29). All bottles should be labeled with a serial number so that no mistake can occur through getting bottles mixed.

The time of starting each test should be so arranged that it will be convenient to take off the bottles at the expiration of the period of agitation. Just before placing the bottle on the agitator, the cyanide solution should be added and the bottle well stoppered.

After the bottle has been agitated for the required length of time, remove from the agitator and allow to settle, then take a 50 cc. sample of the clear supernatant liquid with a pipette, place in an Erlenmeyer flask and titrate as explained later in this article.

WASHING THE RESIDUES.

Wash all the contents of the bottle into the funnel of a vacuum filter, using clear lime water for washing. This serves the double purpose of washing all dissolved values from the residues and preventing inaccurate results due to leaving rich sulphides in the bottom of the bottles.

The use of lime water instead of tap water is to be preferred as it serves to prevent a reverse action taking place, by which the values already in solution might be precipitated in the ore, thus preventing their removal by washing. In washing with lime water special care should be taken to prevent addition of solid lime to the ore, as the ore would be mixed with a barren substance, resulting in the assays being lower than they should be.

Place the washed residue from the suction filter, in a tin pan on a hot plate or radiator. When thoroughly dry, grind in a Wedgewood mortar to break up the lumps, mix on a rubber cloth, sample and assay in duplicate. If in assaying the original ore sample, it was found necessary to grind finer than 100 mesh, grind the residues to the same mesh.

ALKALINITY OF THE SOLUTIONS.

Before giving in detail the method and purpose of titrating the solution sample of each test, it is well to explain the method of expressing the alkalinity in points.

As stated in a previous part of this article (Pahasapa, Vol. IV, No. 1, p. 27), lime is used almost universally as a source of alkali in cyanide work. Lime is therefore taken as the standard, although there are always other alkalies in the solution, such as NaOH and KOH.

Lime is soluble in water or solution to the extent of 0.15% and 1-100 of the lime in a saturated solution is called a "point" of alkalinity. A solution in which there is one-half the possible lime in solution, is said to have 50 points of alkalinity.

Since other alkalies are always present in working solutions, it is possible that the titration may show over 100 points of alkalinity, but it is seldom that this is the case.

In practice, the amount of alkalinity, to insure the best working conditions, is determined by experience and thereafter kept as nearly as possible at that point.

The alkali cyanides, being formed by the combination of a weak acid (CN) and a strong base as K or Na, exhibit strong alkaline properties. Hence, part of the alkalinity of a working solution is due to the cyanides present. This alkalinity can in no way protect the cyanides from the destructive action of cyanicides. It is only the alkalinity, in excess of that due to the cyanides, that can protect them; hence, it is called "protective alkalinity." The alkalinity due to the combined action of the hydroxides, cyanides and one-half of the mono-carbonates is called the "total alkalinity."

TITRATION FOR ALKALINITY.

In practice it is customary to titrate direct for protective alkalinity or for total alkalinity and multiple by some factor which will give the protective alkalinity. This factor is of course determined for any particular plant by repeated tests upon the solution.

The strength of oxalic acid solution used is 14.6069 grams per litre. Ten cc. of a solution of this strength is required to react with 50 cc. of a saturated lime solution; hence, each 1-10 cc. of standard solution, used in titrating 50 cc. of lime solution, represents a "point" of alkalinity.

In 50 cc. of saturated lime solution there is $0.0013 \times 50 = 0.065$ grams CaO. The lime necessary to make one point of alkalinity is in this case 0.00065 grams.

Oxalic acid combines with lime according to:

$$\underset{126}{H_2C_2O_4} + 2H_2O + \underset{56.1}{CaO} = CaC_2O_4 + 3H_2O$$

The oxalic acid to combine with 0.00065 gram CaO is given by x in the proportion:

$$126:56.1::X:0.00065$$

$$x = 0.00146068 \text{ gram.}$$

This weight of acid is to be contained in 1-10 cc. of standard solution; hence, one litre of such a solution will contain 14.6068 grams of oxalic acid.

The following method for determining the total alkalinity is based on that which is thought to be used at the Homestake mine:

To 50 cc. of solution in an Erlenmeyer flask, add a few drops of phenolphthalein and titrate with a standard acid (oxalic) until the color is discharged.

The following method for determining the protective alkalinity is based on a method first suggested by Clennell:

Titrate 50 cc. of clear solution in an Erlenmeyer flask with standard $AgNO_3$ solution, to the first white turbidity. The amount of cc. used divided by 5 gives the cyanide strength in pounds per ton. Then add a few drops of phenolphathalein and titrate with standard oxalic solution (14.6068 grams per litre) until the color is discharged. The number of tenths of a cc. of standard used, represents the points of protective alkalinity.

Objections have been raised against the two methods given above, on the grounds that in the presence of zinc compounds, the results are inaccurate. However, it is believed that if the tests are carried out as directed, the results are sufficiently accurate for technical purposes.

AGITATION SERIES.

In making the agitation tests, several series should be run, each series demonstrating the effect of one varying factor. Starting with a series on 100 mesh ore, the strengths of solution can be raised till a strength which gives the best results is obtained, the tests all being agitated for the same period of time. Using the 100 mesh ore and the best solution strength, the next series can be run having time of agitation as the variable. Having now time and strength of solution determined, a series can be run to find the best size of ore particles. In this series, the remarks previously made, in regard to balancing cost of crushing against increased extraction, should be borne in mind.

SCARCITY OF THYMOL.

According to the Indian Trade Journal there is apparently no great effort being made to meet the demand for thymol that has become so insistent since the German supply was cut off by the war. This opinion is based on the fact that whereas formerly large quantities of ajowan seed *(Carum copticum)* were shipped from India to Germany for the manufacture of thymol, now the shipments are of practically no importance. In June, 1914, 2,032 hundredweights of 112 pounds of ajowan seed were exported from India, and of this total Germany took about 2,000 hundredweights. These figures may be considered to be about the normal monthly average. In April, 1915, the total exports were only 44 hundredweights. The shortage of the drug is well illustrated by the phenomenal increase in price that has taken place since the war started. The normal price in London in average seasons was about $1.25 a pound, but within a month after the outbreak of hostilities it had jumped to nearly $10. This high mark was not maintained after the excitement of the first weeks of the war had subsided, and at the end of April the drug was quoted at $5 to $6 a pound on the London market. Recently, however, there has been another decided rise, the price in New York being quoted at the remarkable figure of $12 on July 12.

ELECTRIC STEEL DIRECT FROM ORE FINES.*

By A. C. DALTON.

The electric furnace is growing of more importance every day in the metallurgical world; its use in the steel foundry has a promising future and its application to the smelting of iron ores is now an everyday occurrence.

Of increasing importance is the application of the electric furnace for the reduction of iron ore into pig steel. To the metallurgist the problem of using low grade ores is one of great and increasing difficulty, since by concentration these ores are usually put into a condition which prohibits their satisfactory use in the blast furnace. Briquetting the cencentrates is expensive and not applicable to all classes of ores, and the cost of it, when added to the mining and transportation charges, makes the ore frequently of little market value.

In localities where cheap electric power and the necessary carbon for reduction are available, it has been hoped that the electric furnace, as it uses no blast, would solve the problem of smelting concentrates and fine ores without briquetting. Through the manufacture of pig steel, it is now possible to smelt successfully ores that were once a waste product of the blast furnace or were too far away from industrial centers to be considered of commercial value. Such conditions exist both in Canada and the United States.

A process that is meeting this situation is that in use at the plant of the Moffat-Irving Steel Works, Ltd., of Toronto, Canada. James W. Moffat has paid considerable attention to the problem of smelting ore fines, and has designed the furnace now in operation at this plant for reducing these ores for the production of pig steel or for direct production of steel castings or ingots.

It is intended to describe in this article only the process for the manufacture of pig steel, because of the interest aroused in it by Prof. J. W. Richards, Messrs. Lyon & Keeney and other prominent authorities in the metallurgy of iron and steel. We have yet a considerable amount of work before us, but in publishing our results at such an early date, we do so under the pressure of many inquiries concerning the operation of the furnace.

The furnace is a 300-kw. one, of the three-phase type. The current is received at 12,200 volts and is stepped down by a three-phase transformer to 80 volts and is conducted to the furnace (which is quite close) by means of the usual copper busbars and by copper cables clamped on to three electrodes, the clamp connections being water-cooled.

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*From The Iron Age.

The electrodes are graphite ones, of Acheson manufacture, and are circular in section of $5\frac{1}{8}$-in. diameter and 40 in. long and are fitted for continuous feed. The electrodes, regulated by hand, enter the furnace at an angle of 65 degrees and are spaced in a delta formation. Bronze water jackets surround the electrodes where they pass through the roof.

The furnace itself may be divided into three parts: the hearth, the reduction chamber and the stack. The hearth, inclosed in a steel shell, is of the tilting type operated by two hydraulic cylinders under the furnace. The lining is the usual basic lining of magnesite and tar, and magnesia bricks; up to the present no trouble has arisen owing to these bricks spalling. The roof of the furnace is acid and of fireclay brick. The combination of the tilting hearth under a fixed reduction chamber constitutes one of the patents covering this furnace. In the center of the roof is an opening registering with a like one in the reduction chamber, and when tilting the hearth the contact is broken at this junction, which, however, is rendered quite air-tight on replacing the furnace.

The reduction chamber, which is of the shape of an inverted cone, is built of firebrick, and opens direct to the stack, where the carbon, ore and flux are fed into the furnace some 13 ft. above the hearth. The ore, carbon and lime are stored in bins at the top of the building, the bins being filled with an endless chain conveyor. From the bottom of these bins the contents are led to hoppers placed at the side of the stack above the reduction chamber. From these hoppers, the materials are separately showered into the hot furnace by means of worm screws, these being controlled by three variable speed cone pulleys driven by a 3-hp. motor. They are so arranged that any single speed may be quickened or slackened independently of the others, thus permitting any desired ratio, or all can be regulated together by changing the speed of the large cone pulley directly connected to the main shaft. Thus it will be seen that there is happily a wide scope for variations of the speeds and ratios.

The furnace being hot from a previous run, about 200 lbs. of scrap is placed in the furnace to form a ready contact, or a like weight of molten metal is left in the furnace from a previous run, and for a few minutes carbon is charged into the furnace to give a reducing atmosphere. The power is then put on and all the materials are fed into the furnace at the predetermined speeds and ratios per hour. When the charge is clearly melted, the slag is withdrawn by tilting the furnace and the metal poured into a ladle and cast into pigs. The process is simplicity itself, and the charge takes the current so steadily that there is little regulating to be done. The melter, being obliged to give practically no attention to the furnace, keeps his eye upon the working of the materials from the bins to the furnace. Owing to the instantaneous action of the hot gases on the fine particles, we have found that when the weighed charge has been completely and properly fed into the furnace it requires only a very few minutes to melt any small remainder of it still visible on the bath, so completely has the reduction taken place in the shower. The ore used in our work was blast furnace flue dust, which had been concentrated by passing it through a Ball & Norton magnetic separator; 60 per cent of the concentrates will pass through a 60-mesh screen, and all will pass a 10-mesh screen. Air slacked lime was used as a flux, and coke breeze for carbon. The materials had the following analyses:

COKE BREEZE.

	Per Cent.
Ash	22.00
Sulphur	1.26
Volatile carbon	6.30
Fixed carbon	71.70

FLUE DUST.

	Per Cent.
Silica, SiO_2	4.80
Ferric oxide, Fe_2O_3	87.36
Ferrous oxide, FeO	3.14
Lime, CaO	0.10
Alumina, Al_2O_3	2.40
Magnesia, MgO	0.30
Manganese oxide, MnO	0.56
Sulphuric acid, SO_3	0.14
Phosphoric acid, P_2O_5	0.115
Carbon, C	0.82
Loss on ignition	0.20
Metallic iron	63.6

LIME.

	Per Cent.
Lime, CaO	54.81
Magnesia, MgO	1.01
Silica, SiO_2	2.08
Phosphoric acid, P_2O_5	0.004

As a basis for our calculations, Grönwalls' formula was used:

$$13Fe_3O_4 + 40C = 39Fe + 28CO + 12CO_2$$

From this equation our quantities were determined and our speed of charging calculated on the best Swedish practice of 1 lb. of metal per kilowatt hour. Taking them as calculated we used:

Flue dust per 1,000 lbs. of iron	1,572 lbs.
Coke dust for reduction	289 lbs.
Lime for fluxing	278 lbs.

RATE OF FEEDS.

1 lb. of metal per kw.-hr., at 250 kw. = 250 lbs. of metal per hour into the furnace; 1,572 lbs. of ore at 393 lbs. per hour would take four hours.

Coke—On the above basis 72 lbs. per hour was used.

Lime—70 lbs. per hour.

In this particular run the materials were all fed into the furnace 20 minutes under the four hours and were all melted except for a small ring round the hearth which when mixed was clearly melted about five minutes afterward. The slag was then poured off and the metal cast into pigs, which gave the following analysis:

Com. carbon	Si.	Mn.	S.	P.
0.02	0.01	Trace	0.131	0.013 per cent.

Another run was made using the same proportions, only the feeds were speeded up to the rate of 1 lb. of metal per ¾ kw-hr., or the equivalent to the reduction of 1,000 lbs. of metal in three hours. This heat was not quite so clearly melted when the ore had been all fed into the furnace, but was completely so inside of the three hours' time. When poured the metal gave the following analysis:

Com. carbon	Si.	Mn.	S.	P.
0.02	0.04	Trace	0.138	0.017 per cent.

Referring to the analyses of the materials charged, it will be noticed that the flue dust is low in sulphur and that the coke is high. The coke introduces 77.3 per cent of all the sulphur entering the furnace, or nearly four-fifths. Had charcoal been used instead, the sulphur would have been reduced to about 0.03 per cent in the pig steel. With this one exception, it will be seen that the metal is of such purity that it is ready for recarburizing and the alloy additions. The reduction of the ore depends upon a rich supply of CO, as the ore is never in contact with the solid carbon. The reactions which take place are rather complex and probably of a double nature. The gas problem, while not having received the immediate attention of Mr. Moffat, has not been overlooked and arrangements are being made to allow air to enter at the top of the reduction chamber to burn the escaping waste gas for the purpose of preheating the ore while being showered through the upper stack.

The success of this process opens a new field in the use of low grade ore after concentration without the further expense of briquetting. This type of furnace will be a natural adjunct of the blast furnace as it will enable all the lump ore to be saved for the blast furnace, while the fines from the calcining kilns and the flue dust may be used for the production of either pig steel or be made direct into steel castings.

Some of the commercial advantages claimed for the process are: It uses concentrates, fines, or sands direct, without admixture with lump ores; the cost of nodulizing or briquetting the ore fines is dispensed with; the purifying of the ore charged (which can now be freely concentrated) reduces the amount of flux required, and thus makes a larger furnace output of metal possible; it is cheaper to take impurities out of the ores by a crushing and concentrating process costing 25c to 50c per ton of crude ore than it is with a process where the electric heat costs $7 to $20 per ton, and the cost of furnace product is materially reduced; in the reducing chamber the small particles of carbon are instantaneously acted upon, and during the reduction there can be no danger of explosion by scaffolding; the rate of speed can be altered instantaneously and the altered rates are immediately effective on the bath itself; the cheaper forms of carbon, such as coke breeze, coal slack and charcoal dust, are used, instead of higher grade qualities; the falling charge does not come into contact with the electrodes; there is no freezing of any descending charge to the walls, should the electric power unexpectedly fail.

RESISTANCE TO CORROSION OF IRON AND STEEL.[*]

A committee of the American Railway Engineering Association has been engaged for two years on a series of tests to determine the relative resistance to corrosion of various samples of iron and steel, and the results are of special interest in view of the widely published claims concerning the resistance to corrosion of certain brands of iron and steel of special chemical composition.

A report of the tests was presented at the annual meeting of the association in March, and, since that time, they have been continued so that the results are now available from a 12-month exposure of the samples. The results indicate that corrosion proceeds at a substantially uniform rate on all kinds of rolled iron and steel, no matter what its composition.

In the tests beginning May 1, 1913, seven samples of iron and steel were selected, as follows:

No. 1. Charcoal iron.

No. 2. Openhearth steel.

No. 3. Openhearth steel, consisting of 0.40 per cent of copper.

No. 4. Openhearth steel, containing 1.00 per cent of copper.

No. 5. Ingot iron.

No. 6. Same as No. 3, except as to preliminary surface preparation.

No. 7. Same as No. 4, except as to premilinary surface preparation.

Each sample included four pieces, each ⅛ in. thick, 2 ins. wide, and 2 to 3 ins. long.

In the following analysis, the figures in the first column are as given by the manufacturers, and in the second by S. W. Parr, Professor of Applied Chemistry:

NO. 1.—CHARCOAL IRON.

	Chemical Analysis by Makers,	Chemical Analysis by Parr, Per Cent.
Carbon	No analysis	0.041
Manganese		0.205
Phosphorous		0.049
Sulphur		0.032
Copper		0.00
Silicon		0.033

NO. 2.—OPEN HEARTH STEEL, MANUFACTURED BY THE CARNEGIE STEEL CO.

	Per Cent.	Per Cent.
Carbon	0.15	0.144
Manganese	0.37	0.394
Phosphorous	0.037	0.038
Sulphur	0.037	0.039
Copper	Trace	0.00
Silicon	0.00	0.036

NO. 3.—OPEN HEARTH STEEL, MANUFACTURED BY THE CARNEGIE STEEL CO.

	Per Cent.	Per Cent.
Carbon	0.12	0.141
Manganese	0.38	0.418
Phosphorous	0.020	0.037
Sulphur	0.032	0.028
Copper	0.40	0.43
Silicon	0.00	0.021

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[*] From American Gas Light Journal.

NO. 4.—OPEN HEARTH STEEL, MANUFACTURED BY THE CARNEGIE STEEL CO.

	Per Cent.	Per Cent.
Carbon	0.15	0.139
Manganese	0.45	0.492
Phosphorous	0.023	0.038
Sulphur	0.033	0.034
Copper	1.00	0.98
Silicon	0.00	0.033

NO. 5.—INGOT IRON, MANUFACTURED BY THE AMERICAN ROLLING MILL CO.

	Per Cent.	Per Cent.
Carbon	0.012	0.030
Manganese	0.025	0.180
Phosphorous	0.006	0.017
Sulphur	0.028	0.056
Copper	0.042	0.00
Oxygen	0.035	0.00
Nitrogen	0.004	0.00
Silicon	Trace	0.014

No. 6. Quality, manufacture and analysis the same as No. 3.

No. 7. Quality, manufacture and analysis the same as No. 4.

Five corrosive mediums were selected as follows:

No. 1. Clean sand.

No. 2. Clay soil, to which 5 per cent of salt by weight was added.

No. 3. A mixture of equal parts of white and black alkali soils.

No. 4. Bituminous coal cinders.

No. 5. Cooking water in the overflow tank from the furnace water jackets of the Copper Queen Consolidated Mining Co., Douglas, Ariz.

Analysis of the corrosive mediums are as follows:

NO. 1.—SAND.

	Per Cent.
Silica	82.31
Oxide of aluminum	9.44
Oxide of iron	2.98
Calcium oxide	1.86
Magnesium oxide	0.45
Oxides of sodium and potassium	3.18
Oxide of manganese	Trace
	100.22

NO. 2.—CLAY SOIL PLUS 5 PER CENT SALT.

	Per Cent.
Water	5.89
Silica	54.34
Oxide of aluminum	14.33
Oxide of iron	3.71
Calcium oxide	5.10
Magnesium oxide	2.15
Oxides of sodium and potassium	10.17
Oxide of manganese	0.11
Sulphuric acid, combined	0.95
Chlorine, combined	2.83
Carbonic acid, combined	2.05
Phosphoric acid, combined	0.16
	101.79

NO. 3.—WHITE AND BLACK ALKALI SOIL.

	Per Cent.
Water	5.10
Silica	48.46
Oxide of aluminum	8.06
Oxide of iron	2.00
Calcium oxide	9.45
Magnesium oxide	1.37
Oxides of sodium and potassium	11.10
Oxide of manganese	0.04
Sulphuric acid, combined	9.64
Chlorine, combined	3.64
Carbonic acid, combined	2.26
Phosphoric acid, combined	0.06
	101.88

NO. 4.—CINDERS.

	Per Cent.
Volatile matter	5.44
Fixed combustion carbon	24.60
Silica	41.06
Oxide of aluminum	24.76
Oxide of iron	1.54
Calcium oxide	1.60
Magnesium oxide	0.42
Oxides of sodium and potassium	1.22
Oxide of manganese	0.02
Sulphuric acid, combined	0.50
Chlorine, combined	Trace
Phosphoric acid, combined	0.07
	101.23

NO. 5.—WATER IN SETTLING TANK.

	Per Cent.
Alkalinity in $CaCO_3$ parts in 100,000	21.00
Hardness in grains per U. S. gallon	3.50
Total solids	57.88
Silica	1.17
Iron oxide and alumina	0.47
Calcium carbonate	0.40
Magnesium carbonate	0.42
Sodium carbonate	14.00
Sodium sulphate	16.80
Sodium chloride	25.20

The sand, clay soil, alkali soil and the cinders were placed in aluminum pans, 4 ins. deep, 11 ins. wide and 16 ins. long in the clear. The pans are numbered 1, 2, 3 and 4, and the settling tank at Douglas, No. 5, corresponding to the numbers designating the corrosive mediums. These pans are kept on the balcony of one of the south windows of the seventh floor of the office building of the El Paso & Southwestern R. R. Co., El Paso, Tex. Exposed to sunlight and air, and the materials in them are periodically saturated with water, thereby being alternately wet and comparatively dry, duplicating in a general way service conditions of iron buried in the ground with a light covering.

In each pan a piece of each sample, No. 1 to No. 7 inclusive, is placed, with the exception of pan No. 5 at Douglas, in which samples Nos. 6 and 7 were not included. The pieces are buried in the corrosive medium by forcing them down edgeways to the middle of the depth of the pan, the pieces standing side by side about 2 ins. apart. As this places one piece of each sample of iron or steel in each pan, it makes the corrosive test strictly comparable throughout for all the corrosive mediums.

Each sample was prepared for the test by carefully filing off all surface oxidation until only clean, bright metal showed over all surfaces, including the edges, with the exception of samples Nos. 6 and 7. The original surfaces of samples 3, 4, 6 and 7, containing copper, were covered with a distinct copper-colored oxidation. This oxidation was left on 6 and 7 to determine its effect in resisting corrosion, as compared with samples Nos. 3 and 4, from which the surface oxidation was completely removed.

After being prepared as above, each sample piece was weighed on a metric scale measuring to 1 centigram, and then immediately immersed in the corrosive mediums. It was decided to clean and weigh the samples at the end of each three months' period, and the loss in weight in grams per square inch of exposed surface was chosen as the unit for corrosive comparison.

It has been found that the corroded samples may be thoroughly cleaned of the corrosive action, leaving the clean metal, by immersing in a 10 per cent solution of ammonium citrate, and this method of cleaning was adopted. In this connection, and at the first cleaning, a clean piece of uncorroded iron was also immersed in the solution in order to determine if the latter itself would produce any loss of weight in the metal. Subsequent weighing of this control piece shows no loss, and the ammonium citrate appears to be a satisfactory medium for cleaning.

In the following tables, the corrosion is measured in loss of weight in grams per square inch of exposed surface and edges:

PAN NO. 1.—CLEAN SAND.

Sample No.	In 3 Mo.	In 6 Mo.	In 9 Mo.	In 12 Mo.
1—Charcoal iron	0.41	0.96	1.34	1.73
2—Carnegie plain O. H. steel	0.42	0.86	1.21	1.56
3—Carnegie 0.4 per cent copper O. H. steel	0.45	0.87	1.24	1.66
4—Carnegie 1.0 per cent copper O. H. steel	0.45	0.90	1.25	1.61
5—Ingot iron	0.43	0.87	1.23	1.61
6—Same as No. 3 not filed	0.34	0.90	1.28	1.61
7—Same as No. 4 not filed	0.31	0.84	1.21	1.58

PAN NO. 2.—CLAY SOIL + 5 PER CENT SALT BY WEIGHT.

Sample No.	In 3 Mo.	In 6 Mo.	In 9 Mo.	In 12 Mo.
1—Charcoal iron	0.13	0.34	0.51	0.85
2—Carnegie plain O. H. steel	0.14	0.32	0.53	0.72
3—Carnegie 0.4 per cent copper O. H. steel	0.20	0.44	0.71	0.95
4—Carnegie 1.0 per cent copper O. H. steel	0.14	0.34	0.60	0.84
5—Ingot iron	0.16	0.41	0.66	0.87
6—Same as No. 3 not filed	0.13	0.35	0.66	0.86
7—Same as No. 4 not filed	0.14	0.32	0.62	0.85

PAN NO. 3.—WHITE AND BLACK ALKALI SOILS.

Sample No.	In 3 Mo.	In 6 Mo.	In 9 Mo.	In 12 Mo.
1—Charcoal iron	0.06	0.13	0.15	0.20
2—Carnegie plain O. H. steel	0.06	0.14	0.16	0.20
3—Carnegie 0.4 per cent copper O. H. steel	0.06	0.14	0.17	0.22
4—Carnegie 1.0 per cent copper O. H. steel	0.06	0.15	0.17	0.22
5—Ingot iron	0.07	0.16	0.18	0.23
6—Same as No. 3 not filed	0.04	0.12	0.18	0.23
7—Same as No. 4 not filed	0.04	0.10	0.15	0.23

PAN NO. 4.—CINDERS.

Sample No.	In 3 Mo.	In 6 Mo.	In 9 Mo.	In 12 Mo.
1—Charcoal iron	0.76	1.23	1.64	2.00
2—Carnegie plain O. H. steel	0.89	1.38	1.73	2.09
3—Carnegie 0.4 per cent copper O. H. steel	0.78	1.34	1.70	2.04
4—Carnegie 1.0 per cent copper O. H. steel	0.78	1.21	1.59	1.93
5—Ingot iron	0.71	1.23	1.60	1.95
6—Same as No. 3 not filed	0.43	0.93	1.29	1.72
7—Same as No. 4 not filed	0.58	1.18	1.59	1.89

PAN NO. 1.—WATER IN OVERFLOW TANK FROM WATER JACKETS.

Sample No.	In 3 Mo.	In 6 Mo.	In 9 Mo.	In 12 Mo.
1—Charcoal iron	1.68	2.188	2.83	3.13
2—Carnegie plain O. H. steel	1.62	2.172	2.76	3.04
3—Carnegie 0.4 per cent copper O. H. steel	1.82	2.310	3.06	3.32
4—Carnegie 1.0 per cent copper O. H. steel	1.77	2.255	3.02	3.28
5—Ingot iron	1.39	1.880	2.65	2.93
6—Same as No. 3 not filed	....	.....	....	....
7—Same as No. 4 not filed	....	.....	....	....

From the results on samples 6 and 7 in pans Nos. 1 to 4, inclusive, it appears that the copper oxidation on the surface, compared with the identical samples Nos. 3 and 4, but with the oxidation removed, protected samples 6 and 7 for 3 months, but the protection appears to have disappeared at the end of 6 months.

PRIZE COMPETITION FOR PAPERS DEALING WITH PROBLEMS IN MANUFACTURE OF PULP AND PAPER.

The technical section of the American Paper and Pulp Association is anxious to bring about advancements in methods of manufacture of paper and pulp, and, with a view of concentrating attention on some of the more important problems before the American pulp and paper manufacturers it offers a prize of $100 for the best paper on each subject in the list given below. It is expected to offer similar prizes each year. This competition is subject to the following rules:

1. The authors of the papers presented must be residents of the United States or Canada.

2. The papers are to reach the office of Thomas J. Keenan, 117 E. 24th St., New York City, the secretary of the section on or before Dec. 31, 1916.

3. Each paper must be typewritten and must not bear the author's name or address. Instead of the author's name the paper shall bear a number or other designating character or word. Accompanying the paper shall be a sealed envelope containing the author's name and address and the number or designating character by which the paper is characterized.

4. Papers presented in this competition must not previously have appeared in print.

5. The determination of the papers winning the prizes shall be made by a committee of three appointed by the chairman of the technical section. This committee shall publicly report its findings to the section at the time of the annual meeting next Feb. 1, 1917.

6. In case papers are not of sufficient merit, the committee shall have the right to omit the bestowal of the prize on any subject for that year, the subject to be carried forward at the option of the committee.

7. All papers received shall be returned to their authors soon after the announcement of the winning paper.

8. The articles winning the prizes offered shall be published in the Report of the Organization and also in "Paper," the official journal of the section.

LIST OF SUBJECTS.

1. The various causes for the deterioration of the Fourdrinier wires and steps to be taken in the prolongation of the life of the wires.

2. How can the pitch in sulphite pulp be eliminated?

3. The effect of the order and time of adding alum, rosin and color in the retention of color.

4. The retention of the various mineral fillers used in paper making and their effect on the life of the machine clothing and the quality of the paper.

PROPOSED TENTATIVE METHODS FOR THE ROUTINE ANALYSIS OF WHITE PIGMENTS.*

METHOD FOR VERY SMALL AMOUNTS OF IRON.

Lead Pigments.—Treat sample with HNO_3 (1:1) in usual manner, dilute with H_2O, add H_2SO_4 to precipitate bulk of lead (not necessary to evaporate down); cool, filter, wash with 1 to 2 per cent of H_2SO_4, make filtrate just alkaline with NH_4OH, then just acid with dilute HNO_3, determine iron colorimetrically by the thiocyanate method, using same amounts of reagents in preparing standards. If sample contains insoluble matter, filter out and wash with hot water till Pb-free, and to filtrate add H_2SO_4 and proceed as given. The insoluble is ignited, treated with HF and H_2SO_4 in usual manner, brought into solution (filter out any $BaSO_4$), and added to filtrate from $PbSO_4$. If necessary, solution may be made up to volume and aliquots taken. Copper, if present, must be removed by precipitating the Fe with NH_4OH, filtering, washing, redissolving $Fe(OH)_3$ and proceeding as above.

Other Pigments.—Treat as above, omitting the addition of H_2SO_4.

GENERAL METHOD.

"Volume" or "apparent" specific gravity shall be determined by the Scott volumeter. True specific gravity shall be determined by Thomson's[1] method, or by means of a 50-cc. pyknometer, using c. p. benzene and 10 to 20 g. of pigment.

BASIC CARBONATE OF LEAD.

Total Lead (Gravimetric).—Dissolve 1 g. in 20 cc. of HNO_3 (1:1) in a covered beaker, heating till all CO_2 is expelled; wash off cover, add 20 cc. of H_2SO_4 (1:1) and evaporate to fumes of SO_3, cool, add about 150 cc. of water and 150 cc. of ethyl alcohol; let stand in *cold* water 1 hour, filter on a Gooch crucible, wash with 95 per cent ethyl alcohol, dry at 110° C., and weigh $PbSO_4$; calculate to PbO or to basic carbonate.[2] Instead of determining the lead as sulphate, the sample may be dissolved by boiling with acetic acid; then dilute to about 200 cc. with water, make alkaline with NH_4OH, then acid with acetic acid, heat to boiling and add 10 to 15 cc. of a 10 per cent solution of potassium dichromate; heat till the yellow precipitate assumes an orange color. Let settle and filter on a Gooch crucible, washing by decantation with hot water till the washings are colorless finally transferring all of the precipitate. Then wash with 95 per cent ethyl alcohol and then ether; dry at 110° C. and weigh $PbCrO_4$. (Any insoluble matter should be filtered out before precipitating the lead.)

Total Lead (Volumetric).—Dissolve 0.5 g. of sample in 10 cc. of concentrated hydrochloric acid, boil till solution is effected, cool, dilute to 40 cc., neutralize with ammonium hydroxide. Add acetic acid until distinctly acid, dilute to 200 cc. with hot water, boil and titrate with ammonium molybdate as follows:

Dissolve 4.25 g. of ammonium molybdate in water and make up to one liter. To standardize this solution, dissolve about 0.2 g. of pure lead foil in nitric acid (pure PbO or $PbSO_4$ may also be used), evaporate nearly to dryness, add 30 cc. of water, then 5 cc. H_2SO_4 (sp. gr. 1.84), cool, and filter. Drop filter with $PbSO_4$ into a flask, add 10 cc. concentrated HCl, boil till completely disintegrated, add 15 cc. of HCl, 25 cc. of water, and NH_4OH till alkaline. Acidify with acetic acid, dilute to 200 cc. with hot water and boil. Titrate, using an outside indicator of one part of tannic acid in 300 parts of water.

It should be noted that when calcium is present, it forms a more or less insoluble molybdate, and results are apt to be high. With samples containing less than 10 per cent of lead, the lead should be precipitated as $PbSO_4$, filtered, redissolved and titrated as in the process of standardizing.

Carbon Dioxide.—Determine by evolution with dilute hydrochloric acid absorbing in soda-lime or KOH solution. Calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

Acetic Acid.[3]—Place 18 g. of the pigment in a 500 cc. flask, add 40 cc. of sirupy phosphoric acid, 18 g. of zinc dust and 50 cc. of water. Connect to a straight Liebig condenser, apply heat and distill down to a small bulk. Then pass steam into the flask until it becomes about half full of condensed water, shut off the steam and distill down to a small bulk—this operation being conducted twice. To the total distillate which was collected in a larger flask add 1 cc. of sirupy phosphoric acid, connect to a Liebig condenser, using a spray trap, and distill to a small volume—about 20 cc. Pass steam through till about 200 cc. of water condense in the distillation flask, shut off steam and continue the distillation. These operations of direct and steam distillations are conducted until 10 cc. of the distillate require only one drop of 0.1

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*Report of Sub-Committee of American Society for Testing Materials.

[1] Proceedings, Am. Soc. Test. Mats., Vol. XIII, p. 407 (1913).

[2] This method of weighing lead sulphate is not accurate in the presence of calcium compounds.

N alkali to give a change in the presence of phenolphthalein. Then titrate the total distillate with 0.1 N sodium hydroxide and phenolphthalein and calculate the total acidity as acetic acid. It will be found convenient to titrate each 200 cc. portion of the distillate as collected.

Metallic Lead.[3]—Weigh 50 g. of the sample into a 400 cc. beaker, add a little water and add slowly 60 cc. of 40 per cent acetic acid and after effervescence has ceased, boil on hot plate. Fill the beaker with water, let settle, and decant the clear solution. To the residue add 100 cc. of a mixture of 360 cc. of strong NH_4OH, 1,080 cc. of water, 2,160 cc. of 80 per cent acetic acid and boil until all solution is complete. Fill beaker with water, let settle and decant the clear solution. Collect residue on a watch glass, floating off everything but metallic lead. Dry and weigh. Result $\times 2 =$ percentage of metallic lead in sample.

The following method of A. N. Finn (unpublished) gives total basicity of a pure white lead: Place 2 g. of pigment in an evolution flask, add a little CO_2-free water, connect up to the separatory funnel and condenser (Knorr type), add through the funnel, finally washing down, 100 cc. of N/4 nitric acid, boil and absorb the CO_2 in soda-lime tube in usual manner (having H_2SO_4 and $CaCl_2$ drying tubes in train) and weigh. To the solution in the evolution flask, add about 20 cc. of neutral sodium-sulphate solution and titrate with N/4 sodium hydroxide solution (carbonate free), using phenolphthalein. CO_2 is calculated to $PbCO_3$. The amount of N/4 acid corresponding to the CO_2 is calculated and deducted from the total amount of N/4 acid neutralized by the sample and the difference calculated to combined H_2O, from which $Pb(OH)_2$ is computed.

BASIC SULPHATE OF LEAD.[4]

Determination of Total Lead.—Dissolve 1 g. of the sample in 100 cc. of a mixture consisting of 125 cc. of 80 per cent acetic acid, 95 cc. of NH_4OH (sp. gr. 0.90) and 100 cc. of water. Add the solution while hot and dilute with about 50 cc. of water, boil until sample is dissolved. Dilute to 200 cc. and titrate with standard ammonium-molybdate solution as described under basic carbonate of lead. The ammonium-molybdate solution contains about 8.67 g. per liter and is standardized against pure lead foil, pure PbO or pure $PbSO_4$.

Determination of Total Zinc.—Boil 1 g. of the sample with 30 cc. of water, 4 g. of NH_4Cl and 6 cc. of concentrated HCl (some $PbSO_4$ or $PbCl_2$ may not dissolve). Dilute to 200 cc. with hot water, add 2 cc. of a saturated solution of sodium thiosulphate and titrate with a standard solution of potassium ferrocyanide in usual manner. Calculate the zinc to ZnO,[5] as follows:

99.70[a]—percentage of ZnO found=percentage of lead constituents; then

$$\frac{\left(\dfrac{\text{Molecular weight } PbSO_4}{\text{Atomic weight Pb}} \times \begin{array}{c}\text{Percentage}\\ \text{of Pb}\\ \text{found}\end{array}\right) - \begin{array}{c}\text{Percentage}\\ \text{of Pb}\\ \text{constituents}\end{array}}{\dfrac{\text{Molecular weight } PbSO_4\text{—Molecular weight PbO}}{\text{Molecular weight PbO}}} = \text{percentage of PbO present.}$$

$$\frac{\left(\dfrac{\text{Molecular weight PbO}}{\text{Atomic weight Pb}} \times \begin{array}{c}\text{Percentage}\\ \text{of Pb}\\ \text{found}\end{array}\right) - \begin{array}{c}\text{Percentage}\\ \text{of Pb}\\ \text{constituents}\end{array}}{\dfrac{\text{Molecular weight PbO—Molecular weight } PbSO_4}{\text{Molecular weight } PbSO_4}} = \text{percentage of } PbSO_4 \text{ present.}$$

Sulphur Dioxide.—Digest 2 g. of the sample with frequent stirring in 100 cc. of freshly boiled *cold* water and 5 cc. of concentrated HCl; let stand 10 to 15 minutes, add an excess of 0.01-normal iodine solution and titrate back with 0.01-normal sodium-thiosulphate solution, using starch indicator. Report as SO_2. Run blank or reagents and making corrections. Or, the SO_2 may be titrated directly with iodine.

Soluble Zinc Sulphate.—Determine as under "Zinc-Lead and Leaded Zincs."

ZINC-LEAD AND LEADED ZINCS (OZLO WHITE).

Total Lead and Zinc.—Dissolve 1 g. of the sample by boiling with 250 cc. of water and 20 cc. of concentrated HNO_3, add 5 cc. of concentrated H_2SO_4, and evaporate to copious fumes of SO_3; cool, add 250 cc. of water, let stand *cold* 1 to 2 hours, filter on Gooch crucible, wash with 1 per cent H_2SO_4, ignite, and weigh as $PbSO_4$. Report as $PbSO_4$. The $PbSO_4$ may be filtered on paper and then dissolved and titrated with ammonium-molybdate solution as described under basic carbonate of lead. Make filtrate from $PbSO_4$ alkaline with NH_4OH, then acid with HCl, add 3 cc. of concentrated HCl, heat to nearly boiling, and titrate the total zinc with potassium-ferrocyanide solution and calculate to ZnO.

Sulphates Other Than Barium Sulphate.—Treat 0.5 g. of the sample with 5 cc. of water, 3 g. of NH_4Cl and 5 cc. of HCl saturated with bromine; digest (covered) on steam bath about 15 minutes, add 25 cc. of water, neutralize with dry Na_2CO_3, and add about 2 g. more, boil 10 to 15 minutes; let settle, dilute with hot water, filter and wash with hot water; redissolve in HCl, reprecipitate as above and wash thoroughly with hot water; acidify united filtrates with HCl, adding a slight excess; boil and add slight excess of 10 per cent barium-chloride solution. Let stand on steam bath 1 hour, filter, wash with hot water, ignite, and weigh $BaSO_4$. Calculate to SO_3 (includes SO_3 formed from SO_2). Or, dissolve 0.5 g. of the sample in 25 cc. of water, 10 cc. of NH_4OH (sp. gr. 0.90) and HCl in slight excess; dilute to about 150 cc. with water and add a piece of aluminum foil which should about cover the bottom of the beaker—this held on bottom by means of a stirring rod. Heat gently till all lead is precipitated, decant through a filter, pressing the lead sponge with a flattened rod, and washing with hot water. Add to the filtrate a little pure bromine water, boil until bromine is expelled, add 15 cc. of 10 per cent barium-chloride solution, let stand on steam bath one hour, filter, wash with hot water, ignite and weigh as $BaSO_4$ (any $Sr.SO_4$ present is not decomposed in this method).[6]

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[3] Thompson's Method, Journal, Soc. Chem. Ind., Vol. 24, p. 487 (1905).

[4] J. A. Schaeffer's Method, Journal of Industrial and Engineering Chemistry, Vol. 6, p. 200 (1914), may be used.

[5] It would probably be more accurate to remove total lead as $PbSO_4$ and titrate the zinc in the filtrate after adding NH_4OH and HCl in usual manner.

[a] This figure (99.70) is the average total percentage of $PbSO_4$, PbO, and ZnO, found in 270 total analyses of basic lead sulphate.

Soluble Zinc Sulphate.—Boil 2 g. of the sample with 150 cc. of water and 50 cc. of 95 per cent alcohol for 30 minutes, filter, and wash with a mixture of alcohol and water (1:3). Heat filtrate to boiling and expel most of the alcohol; then determine SO_3 by usual method of precipitation with $BaCl_2$. Calculate to $ZNSO_4$ and SO_3.

Note.—If sample contains Ca or Mg, the Pb and Zn should be separated by precipitation with H_2S after dissolving in HCl, making alkaline with NH_4OH and acid with acetic acid. The $PbS+ZnS$ is dissolved in dilute HNO_3 and the Pb and Zn determined as above.

Sulphur Dioxide.—Determine as under "Basic Sulphate of Lead."

ZINC OXIDE.

Total Zinc.—Dissolve 0.25 to 0.3 g. in 10 cc. of concentrated HCl and 20 cc. of H_2O, make alkaline with NH_4OH, then acid with HCl, add 3 cc. more of concentrated HCl, dilute to about 250 cc. with H_2O, heat nearly to boiling and titrate with standard potassium-ferrocyanide solution as described by Low.[7] Report as ZnO (includes Cd). Iron, copper or other interfering substances should be first removed as described by Low.

Total Soluble Sulphur.[2]—Moisten a 10-g. sample with water, add a few drops of bromine and then concentrated HCl, boil to expel bromine, filter from any insoluble and wash with hot water. Make alkaline with NH_4OH, then just slightly acid with HCl, heat to boiling and add about 15 cc. of hot barium-chloride solution. Let stand several hours (over night), filter on a weighed Gooch crucible, wash well with hot water, dry, ignite for five minutes, cool and weigh as $BaSO_4$. Calculate to S.

Sulphur Dioxide.[8]—Mix 5 g. of sample with 50 cc. of warm (freshly boiled and then partly cooled) water to an emulsion and pour into a glass-stoppered flask containing 18 cc. of HCl and exactly 25 cc. of 0.1-normal iodine solution, stopper and shake until all the oxide is dissolved. Titrate the excess of iodine as rapidly as possible with 0.1-normal sodium-thiosulphate solution. Calculate to SO_2.

Soluble Zinc Sulphate.—Determine as under "Zinc-Lead and Leaded-Zincs."

LITHOPONE—PONOLITH, JERSEY LILY WHITE, BECTON WHITE, CHARLTON WHITE, ORR'S WHITE.

Insoluble and Total Zinc.—Take 1 g. of the sample in a 200-cc. beaker, add 10 cc. of concentrated HCl, mix, and add in small portions about 1 g. of $KClO_3$, then heat on the steam bath until about half of the liquid is evaporated. Dilute with H_2O, add 5 cc. of dilute H_2SO_4 (1:10); boil, let settle, filter, wash, ignite, cool, and weigh the insoluble which should be only $BaSO_4$; make a qualitative examination for alumina and silica. The insoluble should be examined under the miscroscope for the presence of natural crystallin barytes. Samples may also be examined direct. Make filtrate from insoluble alkaline with NH_4OH, acid with HCl, add 3 cc. of concentrated HCl, dilute to about 250 cc. with H_2O, heat nearly to boiling and titrate with $K_4Fe(CN)_6$ solution as under zinc white. Calculate to Zn.

Zinc Sulphide.[9]—Place 0.5 g. of pigment in evolution flask with about 10 g. of "feathered" or mossy zinc, add 50 cc. of water; insert the stopper carrying a separatory funnel and an exit tube. Run in 50 cc. of concentrated HCl from the funnel, having previously connected the exit tube to two absorption flasks in series; first flask contains 100 cc. of alkaline lead-nitrate solution, second flask, 50 cc. of same as a safety device. After all of the acid has run into the evolution flask, heat slowly, finally boiling until the first appearance of steam in the first absorption flask; disconnect, let the lead sulphide settle, filter, wash with cold water, then with hot water till neutral to litmus paper and washings give no test for lead. The PbS precipitate is dissolved in hot, dilute HNO_3, evaporated to fumes with H_2SO_4 and finally weighed as $PbSO_4$. Calculate PbS or $PbSO_4$ to ZnS.

The alkaline lead solution is made as follows: Into 100 cc. of KOH solution (56 g. in 140 cc. of H_2O) pour a saturated solution of lead nitrate (250 g. in 500 cc. of H_2O) until the precipitate ceases to redissolve, stirring constantly while mixing. About 3 volumes of the lead solution will be required for one of the alkali.

Instead of absorbing the evolved H_2S in alkaline lead-nitrate solution, a solution of 8 g. of cadmium chloride in 250 cc. of water and 150 cc. of NH_4OH (sp. gr. 0.90) may be used. The CdS precipitate may be filtered on a weighed Gooch, washed with water containing a little NH_4OH, dried at 100° C., and weighed. Calculate to ZnS. It is better to filter the

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[6] The solubility of $BaSO_4$ is increased by the presence of aluminium chloride. See J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis," p. 615.

[7] Low, "Technical Methods of Ore Analysis," p. —.

[8] Method of G. L. Rigg.

CdS on a small filter and wash as above, then place filter and precipitate in a beaker and dissolve in HCl and $KClO_3$ (keeping at room temperature at first), filter out any paper pulp or insoluble matter; make filtrate alkaline with NH_4OH, then just acid with HCl, heat to boiling and precipitate with $BaCl_2$ in usual manner. Filter, wash, ignite, and weigh $BaSO_4$. Calculate to ZnS.

For very rapid work the contents of the absorption flask, after all H_2S has been absorbed, may be washed into a vessel with cold water and diluted to about one liter, acidified with concentrated HCl and titrated with standard iodine solution, using starch indicator. (The precipitate should be completely dissolved). The iodine solution is prepared by dissolving about 12.7 g. of pure resumblimed iodine and 18 g. of KI in a little water and then diluting to one liter.

CALCIUM PIGMENTS—WHITING, PARIS WHITE, SPANISH WHITE, AND CHALK.

Make a qualitative examination first; should contain only small amounts of insoluble matter (siliceous), iron, aluminum, sulphur, water or magnesium, and should be approximately 95 per cent $CaCO_3$.

Total Soluble Lime.[10]—Weigh out 0.75 g. of the pigment into a small crucible, ignite cautiously to dull redness to destroy organic matter, cool, transfer to a 400-cc. beaker, add 20 cc. of H_2O, cover, then add 15 cc. of concentrated HCl and 3 or 4 drops of concentrated HNO_3, and boil till all the soluble matter is dissolved and all the CO_2 expelled. Wash off and remove the cover, dilute to about 150 cc. with freshly boiled H_2O, heat to boiling and add dilute NH_4OH (sp. gr. 0.96) carefully until a *slight* permanent precipitate forms. Heat to boiling and add 10 cc. of a 10 per cent solution of oxalic acid; stir until the oxides of iron and aluminum are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 cc. of boiling H_2O and sufficient saturated solution of ammonium oxalate (20 to 25 cc.) to precipitate the lime. Boil and stir for a few moments, remove from the heat, let settle and filter on an 11-cm. filter. Wash 10 times with 10 to 15 cc. portions of hot water. Place beaker in which precipitation was made under the funnel, pierce apex of filter with stirring rod and wash precipitate into beaker with hot water, pour warm dilute H_2SO_4 (1:4) through paper and wash a few times; add about 30 cc. of the dilute H_2SO_4 (1:4), dilute to about 250 cc., heat to 90° C. and titrate at once with standard $KMnO_4$ solution (solution should not be below 60° C. when end-point is reached). The $KMnO_4$ is best standardized against Bureau of Standards sodium oxalate.[11] Calculate to CaO and $CaCO_3$.

Mixed Calcium and Magnesium Carbonates.[12]—Weigh 1 g. of the finely powdered sample into a small porcelain dish, add 25 cc. of normal HCl, cover with a watch glass, and when effervescence has ceased, heat to boiling. Cool and titrate with normal NaOH solution, using methyl orange as indicator.

The calculation is as follows:

One gram $CaO = 35.7$ cc. of normal acid. $CaO \times 1.7844 = CaCO_3$. Subtract number of cubic centimeters of NaOH required from 25, result gives number of cubic centimeters of normal acid corresponding to the $CaCO_3 + MgCO_3$. Multiply the weight of CaO in 1 g. of sample (as found in preceding section on total soluble lime) by 35.7; product gives number of cubic centimeters of normal acid corresponding to the CaO present; subtract from total number of cubic centimeters of acid required by $CaCO_3 + MgCO_3$ and multiply result by 0.042, obtaining weight of $MgCO_3$ in 1 g. of sample. The $MgCO_3$ determined by this process should not differ more than 0.25 per cent from that obtained by more elaborate methods. It is to be noted that this method is a measure of the total alkalinity, and if Ca or Mg are present in other forms than carbonate, a complete analysis would be necessary to give percentages of $CaCO_3$ and $MgCO_3$.

Instead of the above, Newberry's[13] method for the simultaneous determination of calcium and magnesium carbonates may be used.

GYPSUM, TERRA ALBA, PLASTER OF PARIS.

Combined Water and Moisture.—Heat 1 g. of the sample in a covered porcelain crucible on an asbestos plate for 15 minutes, then heat bottom of crucible *dull red* for 10 minutes over a Bunsen burner, remove cover and heat for 30 to 40 minutes at a slightly lower temperature. Cool and weigh rapidly. Repeat to constant weight.

Combined water and moisture may also be determined by heating in an air bath at 200° C. to constant weight.

Insoluble Matter.—Boil 2 to 3 g. of the sample with 20 cc. of concentrated HCl, a few drops of HNO_3, and about 50 cc. of water; evaporate to dryness, boil residue repeatedly with 10 per cent HCl, decanting through a filter; finally transfer to the filter, wash with hot water, ignite and weigh insoluble matter; test for $BaSO_4$. Make a qualitative examination of the filtrate from the insoluble matter to determine if Al, Fe, or Mg are present in abnormal amounts (should be mainly Ca and SO_3). Test a separate portion of the sample for CO_2; if desired determine as under Basic Carbonate of Lead.

BARIUM PIGMENTS—BARYTES OR BARITE, "BLANC FIXE."

Examine microscopically to determine uniformity of grinding, size and angularity of particles, crystallin or amorphous. Should be at least 95 per cent $BaSO_4$.

Loss on Ignition.—Ignite 1 g. of the sample for 30 minutes. Loss may be due to organic matter, mois-

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[9] Evolution Method of W. G. Scott, "White Paints and Painting Material," p. 257; see also Blair, "Chemical Analysis of Iron."

[10] Meade, "Portland Cement," p. —.

[11] Circular No. 40, Bureau of Standards.

[12] J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis," p. 522.

[13] Meade, "Portland Cement"; Mellor, "A Treatise on Quantitative Inorganic Analysis," p. 522; Cement Engineering News, Vol. 15, p. 35 (1903).

ture, combined water and CO_2 (and SO_3 from $CaSO_4$ if present). If loss is appreciable, test for CO_2.

Soluble and Insoluble Matter.—Boil 1 g. with HCl (1:3), filter, wash with hot water, ignite, and weigh insoluble matter. This may be treated with H_2SO_4 and HF in usual manner for SiO_2. In the absence of Al_2O_3 (from silicates) residue is considered as $BaSO_4$. Make qualitative tests of filtrate from the insoluble for Al, Fe, Ca, Mg, SO_3. Test a separate portion of sample qualitatively for CO_2.

SILICA PIGMENTS—SILICA OR SILEX.

Silica or silex should be practically pure SiO_2. A qualitative examination will suffice in most cases with a determination of the loss on treating 1 g. of sample with H_2SO_4 and HF in usual manner.

CHINA CLAY AND ASBESTINE.

A qualitative analysis of China clay to determine if essentially hydrous aluminium silicate is generally all of the chemical tests necessary. Color, fineness, etc., are more important than analysis. Asbestine is tested qualitatively to prove that material is as represented. Color, fineness, etc., are important. Asbestine should be examined under the microscope to note whether it is fibrous or talcose and whether silica or china clay are admixed. Samples of known origin should be used here as a guide for comparison.

REACTIONS OF SILKS MADE FROM CELLULOSE.[*]

Viscose compounds of sulphite cellulose are constantly increasing in variety and use. They range from the higher grades of artificial silk to sausage casings and a special form of tissue paper. It is a matter of importance for cellulose and paper chemists to be able to identify with certainty the important kinds of artificial silks met with in commerce. A step in the direction of assembling tests and identity reactions has been taken by Dr. Louis J. Matos, who contributes an article on the subject to the *American Silk Journal.*

Referring to the difficulties experienced by dyers of artificial silk compounds, he observes that many instances are familiar to dyers where lots of mived artificial silk have been sent to the dyehouse, and inequality in dyeing was not discovered until near the end of the operation, when it became a matter of great skill to bring up the shade of the indifferent skeins to the shade of the main lot. This condition could have been anticipated had the dyer been acquainted with the fact that the entire lot of silk was not of one kind.

From time to time there have been published tests and reactions with chemicals to be used in distinguishing the several kinds of artificial silks, but the practical application of which, in the dyehouse or office, seems to offer some obstacles in the hands of those not actually acquainted with the details of making reactions. It seems that while the method of making the tests is simple enough, the greatest difficulty is in having the solutions or reagents properly compounded and in conducting the tests afterwards.

Simple descriptions alone do not seem to meet the case entirely. Of course, there is nothing to take the place of a practical demonstration of a testing method when carried out by one who is practically familiar with the proper sequence of the operations. On the other hand, many of the methods for fiber testing that have been published, while apparently intended for dyers and practical mill men, being those most concerned, are, as a rule, written for the chemist with some experience, as only such could possibly have the unusual reagents and apparatus, or even the apparently delicate manipulative skill, to handle both satisfactorily.

Without question, the most satisfactory means to identify artificial silk is to make use of the microscope, but as very few mills are equipped with this valuable instrument, and fewer still are proficient in making use of it, we will omit its discussion as applied to artificial silk and confine ourselves exclusively to the chemical or *wet methods* that experience has taught us are the most satisfactorily. To identify artificial silk properly requires that the person attempting the work should have at hand a small set of chemical reagent bottles of not more than two-ounce capacity and with glass stoppers. Such bottles are not costly and may be obtained through a local druggist; the style known as "XX Tinctures" are admirably suited for the purpose. They are to be filled with the following reagents, which can be procured from a chemical supply house or prepared by a friendly pharmacist or chemical friend. The following constitutes the list and the methods for their preparation:

No. 1. *Glycerinated Sulphuric Acid.*

Pure glycerin	10 Cc.
Distilled water	5 Cc.

Add slowly with constant stirring, a few drops at a time, pure concentrated sulphuric acid—15 Cc.

No. 2. *Iodoiodide of Potassium.*

Distilled water	30 Cc.
Potassium iodide	0.3 Gm.

Iodide, an excess.

No. 3. *Chloriodide of Zinc.*

Distilled water	30 Cc.
Fused chloride of zinc	1.75 Gm.

Filter and add to clear filtrate iodine to saturation.

No. 4. *Cold concentrated sulphuric acid.*

No. 5. *Half saturated chromic acid.*

No. 6. *A 40 per cent caustic potash solution.*

No. 7. *Copper oxide-ammonia.*

Ammonium-copper oxide is an important reagent in all fiber work. It should be made with great care by preparing a solution of copper oxide in ammonia to saturation, and passing through it a current of air freed from carbon dioxide, by first being passed through a solution of caustic potash.

No. 8. *Nickel oxide ammonia.*

Nickel sulphate in crystals	2 Gm.
Water	30 Cc.

Precipitate the nickel with caustic soda and filter; then dissolve the precipitate in a mixtrue of:

Concentrated ammonia	8 Cc.
Water	8 Cc.

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[*] From Paper.

No. 9. *Alkaline copper glycerin solution.*

Sulphate of copper	3 Gm.
Water	30 Cc.
Glycerin	1.75 Gm.

to which is added a sufficient quantity of caustic potash solution to precipitate the copper and redissolve it.

No. 10. *Diphenylamine-sulphuric acid solution.*

Diphenylamine	1.57 Gm.
Concentrated sulphuric acid	25 Cc.

The operator should keep these bottles in a closet when not in use and at all times free from dust. The label, besides the name, should also have the formula written upon it.

The apparatus required to make the tests consists of a dozen small plain white butter dishes, a dozen small test tubes of short length and not over half an inch in diameter, and a spirit lamp or bunsen burner to supply heat. There should also be at hand two small bottles or tubes containing red and blue litmus paper. The entire outfit is procurable under five dollars.

There are five kinds of artificial silk generally met with in commerce, as follows: Collodium silk (strictly nitro silks), cellulose silks, viscose silks, acetate silks, gelatin silks.

The first important test to make is to determine whether the silk under examination is made from gelatin or not.

Take one of the test tubes, see that it is clean and dry inside, and place at the bottom of it a small tuft of the silk about the size of a small pea when rolled between the fingers. In the open end of the tube insert a piece of red litmus paper, bending the end over so that the strip will not slide down the tube. With a handle made of several folds of paper around the neck of the tube so as to permit one to hold it comfortably, place the closed end of the tube in the flame of the bunsen burner or spirit lamp, giving the tube a slight to-and-fro motion until the fibers in the tube begin to char and vapors are seen to arise. When these vapors are observed to come out of the open end of the test tube, note whether the color of the red litmus paper changes to blue. If such a change takes place it is due to the presence of ammonia gas resulting from the charring of the fibers and which could only come from gelatin silk. These vapors may also have the odor of burning horn or hair, which odor is further indicative of the presence of gelatin.

On the other hand, if the litmus paper does not change color, acid fumes may be present and are to be confirmed by repeating the test, but using *blue* litmus paper, which, upon turning red, indicates that the silk may be any one of the four makes named. To distinguish finally between the several artificial silks emitting acid fumes with heat, place two of the butter dishes side by side; in one, place some of the silk fiber and upon it pour some of reagent No. 1, and let soak for a few minutes, and then afterwards add a few drops of reagent No. 2. In the second dish put some of the fiber and a small amount of reagent No. 3, and note carefully what changes in color, if any, take place. If both samples show a distinct yellow coloration, the silk is *acetate silk*.

On the other hand, if the coloration is blue, the silk may be either *collodium*, *cellulose*, or *viscose silk*, which is confirmed if the coloration shown in the second dish is reddish-violet. To differentiate between these three silks just mentioned, place a small tuft of the fibers in a dry dish and pour upon it a small amount of cold concentrated sulphuric acid (No. 4). If the silk dissolves rapidly, the specimen is either collodium or viscose silk; cellulose silk, i. e., Pauly, Fremery, etc., dissolves slowly.

Confirmatory tests are made in test tubes with the chromic acid solution (No. 5) in the cold, when these three silks dissolve gradually, and upon the tube being heated, dissolve quickly. When treated in the same manner with warm caustic potash solution (No. 6) these three silks, together with the acetate silk, show a distinct swelling, while *gelatin silk* dissolves rapidly and completely.

The copper oxide ammonia test (No. 7) when applied in a test tube first causes a swelling and dissolves collodium and viscose silks, but acetate silk swells without dissolving, and gelatin silk takes a bluish-violet coloration without dissolving.

The nickel-oxide-ammonia reagent (No. 8), when applied both cold and warm to a sample of artificial silk in the test tube, causes a swelling of the fibers but without dissolving them. This applies to collodium, cellulose, viscose, and acetate silk, but not to gelatin silk, which latter takes a brown coloration without dissolving.

The alkaline-copper-glycerin solution (No. 9) has no action even after long boiling upon the first four silks above mentioned, but gelatin silk dissolves after a short time.

A convenient reagent for artificial silk is the concentrated sulphuric acid-diphenylamine solution (No. 10), which has been extolled as the one reagent for this class of work, but as a matter of fact its usefulness is limited exclusively to differentiate only the nitro silks from the others. With nitro silks of the Chardonnet type it causes a distinct blue coloration, while the other silks remain uncolored. This diphenylamine reaction lasts but a comparatively short time, reaching its maximum intensity within five minutes after adding the reagent, when it gradually disappears.

In order to be in the position where one can absolutely and certainly pass judgment upon the identity of a given silk sample, the operator should have at hand a collection of true type samples obtained directly from the artificial silk manufacturers and to make the foregoing outlined reactions repeatedly, systematically, and with care. By care is meant not being too hasty in forming a conclusion, and to disregard and reject completely any test that one may have made into which the element of doubt enters. With such a set of proved samples at hand and a set of reagents as above outlined, when unusual lots are received by the dyehouse, or where silk is received from unfamiliar sources, its identity can be accurately determined.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

$400 In Prizes.

A foretaste of the value of the technical section of the American Paper and Pulp Association to manufacturers of pulp and paper is given in the announcement, on another page, of the prizes offered for the solution of important problems confronting all manufacturers. It will be seen from the terms of the prize competition that every precaution has been taken to insure the utmost fairness in the treatment of the essays submitted and the awarding of the prizes. The committee of award will have no clue to the identity of the author of any paper submitted until the award has been made and the sealed envelope containing the author's name and address and the number or designating character by which the paper is marked shall be opened. A careful reading of the preliminary announcement of the committee published elsewhere in this issue is commended to all interested. It is to be hoped that the competition will draw out a large number of papers from technical men and that some of these will be adjudged sufficiently meritorious for the awarding of prizes.

Industrial Research.*

Industrial research is a relatively new thing. It means the co-operation of business and science for their mutual advantage. Not so very many years ago such co-operation would have been unthinkable. To the average business man, the scientist seemed a rather futile fellow whose putterings with test tubes had little more practical value than the researches of a classical scholar in the Greek Dative, while the man of science, like his classical brother, looked with some contempt on the sordidness of trade, talked of "pure" science, as something nobler than "applied" science, and felt that he was losing caste if he permitted his work to suffer contact with "commercialism."

Happily for both business and science, those ideas are now dead—as dead as witchcraft, or the divine right of kings. Repeated object lessons have taught the business man that nearly every marked advance in science has resulted, sooner or later, directly or indirectly, in important effects on industry, while the increasing dependence of modern life on its complex industrial organization has forced the scientist to realize that in benefiting industry he is contributing efficiently to the welfare of mankind, which is, and always must be, the chief aim of all work that is worth while.

The result of this awakening was that business resolved to domesticate science, and that science graciously accepted the home, with all modern improvements, which was offered her. Thus arose the research laboratory of the large industrial corporation.

Though such laboratories have been in existence relatively few years, they have already proved their value. They have been a potent factor in Germany's wonderful commercial development.

The extent to which research has permeated, and made itself an essential part of Germany industry is clearly revealed in the address delivered by Dr. Carl Duisberg before the Eighth International Congress of Applied Chemistry, entitled, "The Latest Achievements and Problems of the Chemical Industry." The scope of the paper is almost co-extensive with industry itself. Production of power, refrigeration, the manufacture of quartz, steel, special alloys of most diverse properties, acids and other reagents, tin, rare metals, and coal tar products including explosives, dyestuffs, and medicinal drugs, chemotherapy, or the treatment of infectious diseases by chemical means, the production of synthetic perfumes, artificial silk, cinematograph films, non-inflammable celluloid and its applications, including patent leather, artificial leather, insulation, enamels, etc., and synthetic rubber —each of these is cited to illustrate notable recent achievements of chemical research.

The coal tar dye industry is built entirely on chemical research. Dr. B. C. Hesse, in the *Journal of Industrial Chemistry*, Dec., 1914, estimates the annual production of dyes in Germany at $68,222,846, more than eleven times the production in Great Britain and about eighteen times the production in the United States. In explanation of this fact he quotes a prominent German chemist as saying, in part, "In no country on earth are those branches of the chemical industry which demand versatility of thought, and particularly a large body of scientifically trained employees, so well developed as with us."

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*From an article by L. A. Hawkins, Engineer, Research Library, General Electric Co., in the General Electric Review.

Germany was the first country to perceive the enormous monetary value of organized industrial research, and great have been the rewards of her foresight.

We, in this country, have been late in starting, but progress has been rapid and the results important. An article by Mr. A. D. Little in the *Journal of Industrial and Engineering Chemistry*, Oct., 1913, entitled "Industrial Research in America," is an impressive exposition of the extent to which organized science has already become a business asset in the United States. For instances, he cites the DuPont Powder Co., employing 250 trained chemists, with a laboratory comprising 76 buildings spread over 60 acres, which estimates that its laboratory yields an annual profit of $1,000,000; the world famous Edison laboratories with their multifarious important products; the automobile industry, in which one tire manufacturer spends $100,000 a year on his laboratory; the Bausch & Lomb Optical Co.; the Eastman Kodak Co.; the electro-chemical industries at Niagara Falls; the metallurgical industries, etc., all investing largely in organized research and all reaping profits from their investments.

In all this work, the public benefits, whether by new devices capable of new results, by more efficient apparatus, by better materials, by cheaper goods, or by increase of scientific knowledge. Indeed one of the important advantages the public derives from the existence of the big industrial corporation is the result of industrial research, made possible only by large aggregations of capital, controlled by far-sighted, broad-minded men; for the maintenance of a well equipped laboratory with a capable staff is an expensive matter, and the financial returns are seldom immediate. Years of costly failure must often precede success, and not even then is success always possible. But in the end, industrial research, if wisely organized and efficiently conducted, does pay, and both the corporation and the public benefit.

The New Laboratory of the Pennsylvania R. R.

At the sixth general session of the American Society of Testing Materials, a paper was presented by C. D. Young, engineer of tests of the Pennsylvania R. R., describing the large new physical and chemical laboratory of that railroad at Altoona, Pa. The scope of the work done by the various testing departments of this large railroad was represented by the statement that the cost of the materials covered by the inspection and tests and entering into the construction of the railroad rolling stock and track in 1913 amounted to $82,119,480, while the cost of operating the test department and chemical laboratory for the same year was $534,060. Using these figures for an approximation, Mr. Young stated that it was interesting to observe that the total cost of operating the departments, including all additional work and instruction, is about 0.6 per cent of the cost. In 1913 there were 61,148 separate reports of material tests issued by the test department and 138,896 tests made in the physical laboratory. In the chemical laboratory in 1913 a total of 57,309 samples were analyzed, involving about 286,545 determinations. An important addition to this railroad's testing equipment is the laboratory car which is moved to points where steel rails are to be inspected in process of manufacture. The object is to make chemical analyses of the finished rails at the mills by a force of chemists under the chief chemist so as to avoid delay. The car is equipped with furnaces for combustion and all other necessary apparatus.

New Publications of Bureau of Mines.

The following is a list of the new publications of the Bureau of Mines, Department of the Interior, Washington, D. C.:

Bulletin 72. Occurrence of explosive gases in coal mines, by N. H. Darton, 1915. 248 pp., 7 pls., 33 figs.

Technical Paper 84. Methods of preventing and limiting explosions in coal mines, by George S. Rice and L. M. Jones. 1915. 43 pp., 14 pls., 5 figs.

Technical Paper 88. The radium-uranium ratio in carnotites, by S. C. Lind and C. F. Whittemore. 1915. 29 pp., 1 pl., 4 figs.

Technical Paper 100. Permissible explosives tested prior to March 1, 1915, by S. P. Howell. 1915. 16 pp.

Technical Paper 118. Coke-oven accidents in the United States during the calendar years 1913 and 1914, compiled by A. H. Fay. 1915. 16 pp.

Successful attempts according to the Scientific American have recently been made to manufacture a substitute for rubber tubing out of masses of solidified glue. These tubes, whose trade name is "Sonjatin," are even better than those of rubber for certain purposes, since they are more impervious to gases and more resistant to heat. It is also claimed that they do not grow rotten so quickly as rubber and that when incased in a suitable envelope they will withstand high pressure. Moreover, they are very cheap, gas tubes of the new material costing only 60 pfennig per meter (4.35 cents per foot). The inventor is Prof. J. Traube, and he states that they are peculiarly suited for conductors of petroleum and gasoline as well as gases. However, they are attacked by water, which, obviously, limits their uses.

POSITION WANTED as assistant chemist. Completed the I. C. S. General Chemistry Course and the manufacture of sulphur and hydrochloric acid. Married. Have a responsible position in another line of work; desire a change. Box 6, Chemical Engineer, Chicago, Ill.

The Chemical Engineer

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POTASH PRODUCTION IN CALIFORNIA.*

With the cessation in the customary import of potash salts from Germany and the danger of this interruption being prolonged indefinitely, there is renewed interest in the possibility of securing a supply of the much-needed compounds from domestic sources, and especially from our Pacific States.

Attempts to develop a domestic potash industry are more advanced in California than in any other section. No less than six companies are actively engaged in this field.

MINERAL SOURCES.

Two companies are seeking to extract potash from mineral deposits within the state. These deposits contain frequently relatively high percentages of potash, but not sufficiently high to warrant transportation without previous concentration. This factor of transportation presents the most serious difficulty in the whole problem, as the chief demand for potash as a fertilizer comes from the eastern half of the country, and very largely from the Gulf States. The California State Board of Mines expresses strong doubts as to a possible profitable exploitation of the deposits in the southeastern section of the state on account of their remoteness from existing conveniences for transportation.

The most promising source of potash is in the saline deposits at Searles Lake in San Bernardino County, where the American Trona Co. has erected a development plant and is actively investigating the methods proposed for effecting a complete commercial utilization of the vast supply of raw material in sight. The deposits are not only rich in potash but contain, also, borax, common salt, sodium sulphate, and sodium carbonate. The manager of the company is hopeful of putting potash salts on the market within a few months.

Deposits in the Imperial Valley, to the east of San Diego, are reported as offering some hope of satisfactory commercial development, when projected rail connection is established in 1916.

One California company, which has expended $150,000 in studying the possibilities of finding potash in workable quantities in Nevada, has abandoned the quest and reports that there is no promise of ever securing a supply from that state.

POTASH FROM ALUNITE.

It is worthy of note in this connection that active experiments have been conducted by large chemical works in Ohio for the industrial extraction of the potash present in the alunite of Marysville, Utah. These experiments, performed on carload lots, show that the method used is technically satisfactory. The high cost of railroad transportation from Utah to the Atlantic Seaboard is at present a serious obtsacle in marketing the sulphate of potash obtained in Utah, in direct competition with potash salts of German origin, on the basis of the rates hitherto current. The erection of the requisite plant at Marysville for extracting the sulphate has been begun, and it is probable that a suitable market will eventually be formed for the product in the Central States. There is a large consumption of potash salts in the sugar plantations of Hawaii, and this market would also be open to the Utah products. It is stated that powerful fertilizer interests in Chicago are backing financially the effort to exploit the alunite deposits of Utah.

POTASH SALTS FROM KELP.

The utilization of the enormous masses of seaweed growing off the Pacific coast seems to offer better chances of solving the potash problem. Considerable doubt is expressed by engineers, who have carefully studied the methods thus far employed to develop the kelp industry, as to the possibility of its becoming a serious factor in the production of potash salts.

The leading company engaged in the extraction from kelp is, however, quite confident of its ability to build up the industry on a substantial commercial basis. It is now manufacturing regularly a crude potassium chloride ranging in strength from 85 to 95 per cent of pure KCl. This is all sold for use as a fertilizer. The present output is 1 ton per day. Prospective enlargement of the plant will double this output.

HARVESTING KELP.

The raw material, the giant kelp of the Pacific coast, is gathered systematically in various ways. One method is to cut the kelp 6 to 8 feet below the surface of the sea by means of rotating knives. The loosened kelp is allowed to float ashore or brought ashore in barges. By another method the cutting is effected by the aid of reciprocating knives 16 to 18 inches below the surface, and the kelp is conveyed by endless chains upon barges. In a third method the cutting takes place at a depth of 8 to 10 feet. Horizontal knives are used in connection with an underswinging endless chain.

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*From the Daily Commerce Reports of the U. S. Bureau of Foreign and Domestic Commerce.

The most satisfactory device is based upon the principle of the ordinary hay mower. A horizontal scythe blade, of about 10 feet in length, is flanked at both extremities by vertical blades, about 4 feet long. The three cutting systems, having a stroke of about 4 inches, are operated by a gasoline engine on a flat-decked barge. The framework supporting the cutting machinery is lowered into the water to a depth of about 4 feet. It carries an endless belt consisting of coarse fish net stretched over chains. This conveys the kelp as fast as it is cut on board the barge. A motor launch propels the latter through the kelp beds at the rate of 4 miles per hour.

On the barge the kelp is discharged from the endless belt into a hopper and passes through a set of revolving knives, which cut it into small pieces about 6 inches in length. From this chopper the kelp is discharged into an open barge, which is towed ashore and unloaded at the factory. Such a device harvests over 25 tons of kelp per hour and seems to have satisfactorily solved the problem of the economic gathering of the raw material. The entire cost per ton of wet kelp landed at factories is now less than 20 cents.

DIRECT USE OF KELP.

Wet kelp contains on an average 4 per cent of potassium chlorid. It can advantageously be used as a fertilizer, and is so used to an increasing extent along the Pacific littoral.

Air-dried kelp contains about 15 per cent of potash (K_2O), 2 per cent of nitrogen, and 1.5 per cent of phosphoric acid. It is readily pulverized and is of equal value as a fertilizer with equivalent amounts of potash in the customary form of chlorid and sulphate. Taking all factors into consideration—cost of production, cost of handling and physical properties—dried powdered kelp seems to be the form in which a substantial commercial demand can be most quickly secured. It will rapidly appeal to the manufacturer of mixed fertilizers.

PREPARATION OF POTASH SALTS FROM KELP.

There is as yet no standard method for extracting the potassium chloride of kelp on an industrially profitable scale. The American Potash Co., which has a plant of some size at Long Beach, uses a "secret process," by which it expects to place upon the market iodine and various other by-products, as well as technically pure potassium chloride.

In kelp potassium chloride and sodium chloride are present usually in the proportions of 3 to 2. They constitute the bulk of the mineral constituents, but are accompanied by small amounts of calcium and magnesium salts and of iodides. The separation of the two cholorides from the organic residue constitutes the chief difficulty to be overcome.

Filtration methods applied to green kelp have not been successful, as the absence of fiber permits much of the organic matter to pass through the filter medium, causing the latter to be quickly clogged. Diffusion methods, similar to those used so satisfactorily in sugar manufacture, have been tried. Thus far they give no promise of industrial application.

More success is indicated by experiments now in progress to coagulate the organic tissues of kelp, and thus permit easy filtration.

It is worthy of note in this connection that a process recently patented in Great Britain offers a new method of overcoming the difficulty mentioned above. According to the British Patent No. 1,766 of 1915 issued to Beborg, Testrup and Techno-Chemical Laboratory, kelp is reduced to pulp, and then forced by pressure through a heater at a temperature sufficiently high to destroy the slimy, water-binding constituents. The pulp is then cooled and pressed. In the effluent water are found nearly all of the potassium and sodium salts originally present in the kelp, as well as the iodides.

Once removed from the plant, the separation of potassium chloride from sodium chloride is comparatively easy. It is based upon the fact that the potassium salt is much more soluble in boiling water than is the sodium salt, while the reverse is the case at ordinary temperatures. Alternate crystallizations of saturated solutions, first in a hot vat and then in a cool vat, would result in the accumulation of potassium chloride in the latter and of sodium chloride in the former. Concentrated mother liquors could be treated for the recovery of iodine.

Assuming a satisfactory solution of the coagulation problem, this combined industry would produce pure potassium chloride, pure sodium chloride (table salt), potassium iodide, and a cattle food from the residual kelp, containing 4.5 per cent nitrogen.

EXTENT OF THE KELP SUPPLY.

The area of the kelp beds along our Pacific coast, including Alaska, is nearly 400 square miles. It is estimated by Government experts that the annual cuttings, including two cuttings per annum off the coast of southwestern California, would yield 59,000,000 tons of kelp. This is equivalent to 2,300,000 tons of postassium chloride.

The value of this quantity of potassium chloride, if marketed at current rates, would be about $90,000,000. If, however, the kelp crop were dried and sold at current prices for both potash and nitrogen content, its value would exceed $150,000,000.

The imports into the United States of potash salts for the fiscal year ending June 30, 1914, were:

	Tons.	Value.
Muriate of potash (potassium chloride).	237,890	$7,915,000
Carbonate of potash	92,000	615,000
Sulphate of potash	45,140	1,898,000
Nitrate of potash (crude saltpeter)......	1,580	115,000
Kainit	526,000	2,580,000
Manure salts	261,000	2,757,000
Other potash compounds	......	978,000
Total	......	$16,858,000

It is evident that any extended successful development of the industrial extraction of potash salts from the vast kelp beds would ultimately place this country in a position to cover not only the large domestic demand for these compounds, but to meet German competition in other lands, more especially in supplying the wants of countries on the Pacific.

GROWING SCARCITY OF POTASH SALTS.

The "potash famine" is already being felt almost as keenly as the "dyestuff famine." Since February 1 but one cargo of German potash has been received in an American port. In the meantime the demands of fertilizer works for their customary supplies have become increasingly insistent.

Potash salts, which sold currently a year ago at $38 per ton, are now quoted at $160 to $175. Over 20,000 tons of potash salts, the property of American firms purchased before the recent embargo on German exports, are now interned on three steamers in German ports. The release of these cargoes is the subject of negotiations between the American and German Governments.

EXTERNAL CORROSION OF CAST IRON PIPE*

Cast iron pipe is in such general use that a knowledge of its strong points, its limitations and the precautions necessary to insure its durability under certain conditions, is of the highest importance to the engineer.

There is no limit to the life of cast iron pipe, says a recent advertisement in a technical journal, and this undoubtedly voices the opinion of many well-informed persons. Opposed to that we find the following: "The relatively high rate of self-corrosion (as distinguished from electrolytic corrosion) of cast iron as compared to the other kinds of iron tested, is contrary to the generally accepted idea that cast iron is more resistant to self-corrosion than wrought iron.

We cannot go back very far in our study of cast-iron pipe. The earliest authentic records relate to pipes laid, by order of Louis XIV, near Paris, from the reservoirs of Picardie to those of Montbauron, supplying the town and parks of Versailles. According to the Ministry of Public Instruction and Art, these were laid between 1664 and 1688, and aggregate about 8,000 m. (26,000 ft.) in length, and are still in use.

All of these pipe lines consist of pipes one meter in length, joined by bolted flanges. They are of considerable weight, and still serve their purpose satisfactorily.

The few repairs that have been required generally were necessitated by rusted out bolts.

At Clermont-Ferrand, Department of Puy-de-Dome, in 1746 the Commissioners of Fountains made an agreement with a Parisian iron merchant for furnishing about a mile of 5" or 6" cast iron pipe to supply water to the fountains. The lower portion, in the plain, was under quite heavy pressure, and was 8/10" thick; where the pressure was less, the thickness was only ½". These pipes were in 3-ft. lengths, flanged, and with a lead gasket sometimes as thick as ⅞". In 1867, the system was paralleled by new mains, but much of the original pipe is still in use. At Saint Etienne, in 1904, there were cast iron pipes that had been in service since 1782. A few years ago, the City of Paris abandoned the Chaillot Pumping Station, the first erected for supplying that city with water. The intake of flanged cast iron pipe, extending out into the Seine, was removed, after having been immersed in the river for more than a century. The pipes were found to be so well preserved that they could readily have been used again. The metal was a gray, cast iron of excellent quality. No alterations of either the interior or exterior appeared after its 100 years of service, and fractures were as sharp as those from a fresh casting.

London and Glasgow have a record of 120 years of service for cast iron pipe. The first extensive works in the former city were built by Sir Hugh Middleton, between 1609 and 1613. As early as 1766, the Chelsea Water Company of London, laid a 12" flanged, cast iron pipe, which was relaid in 1791 on account of the joints "being perished." It was the engineer of that water company, Mr. Thomas Simpson, who designed the first bell and spigot pipes about 1785, at which time an experimental section with lead joints was laid. As a rule, however, London was supplied with water through wooden pipes until about 1820.

In the United States, the earliest pipes were of bored logs. Philadelphia adopted them, although, in 1804, about ¾ mile of iron pipe was laid as an experiment. The new Fairmount Water Works in that city had a distribution system of cast iron pipes, the first in America on an extensive scale. These pipes were imported from England, and were of the bell and spigot type, in 9-ft. lengths. A curious feature about them was that each length had three or four ribs or rings about it, approximately 1½" wide, presumably to afford places with heavier walls in which to tap. These pipes are still in use after 95 years. Though forming only an infinitesimal portion of the present distribution system, they, nevertheless, constitute quite a considerable mileage. A few of them are noted to give an idea of their character. A 4½" cast iron pipe on Chestnut street, from Broad to 15th street, laid in 1817, was removed only recently. A 22" main leads from Fairmount Basin to Green street, to Pennsylvania avenue, to Callowhill street; then reduces to 20" to Broad street and thence to Chestnut street. This pipe was laid in 1819, and, with the exception of a portion removed in 1897 on account of the construction of the Pennsylvania Subway, is still in use. Mains on Market street, from Juniper to Broad streets, laid in 1820, from Eleventh street to Juniper street, laid in 1823, and from Water street to Eleventh street, laid in 1822, were in good condition when removed in 1907 for the Market street subway. Mains 6" and 10" in diameter, on Second street, between Greenwich street and Lehigh avenue, laid between 1823 and 1852; 8" mains on Front street, between Wharton street and Laurel street, laid at various dates between 1822 and 1834; one 10" main on Chestnut street, from Front street to Broad street, laid in 1821 and 1823; and a 20" main on Fifteenth street, from Callowhill street to Chestnut street, was laid in 1829. All these mains are still in use.

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*From a paper by Marshall R. Pugh, presented before the American Society of Civil Engineers and printed in Vol. XL of the Proceedings, pp. 1641-1691.

The late James B. Francis, Past-President Am. Soc. C. E., cited the case of Lowell, Mass.:

> It is within my experience and knowledge that pipes at Lowell, obtained from Philadelphia in 1830, were intended for use under a pressure of 150 feet head, and are now in use under 200 feet head, without any signs of failure after 60 years.

Even when immersed in the fresh water of streams and rivers, this resistance to corrosion is manifested. Cast iron cannon taken from a vessel sunk in the Delaware River for more than 40 years, were perfectly free from rust.

Summing up what has been observed, it may be said that our experience of 250 years with cast iron pipe has not been sufficiently long to establish just what its life is.

EXAMPLES OF DETERIORATION OF CAST IRON PIPE.

One of the earliest observations of rapid deterioration of cast iron pipe is that of Mr. Thomas Duncan, who, in 1853, in describing the Liverpool Corporation Water Works, said:

> During the process of taking up and adjusting the pipes in the district near the margin of the docks, where the soil is impregnated with salt, they were found, in many instances, to have become so soft that they could easily be cut by a knife. These had not been laid more than twenty years; whereas, in the higher districts, where laid nearly fifty years, they were found to be as good as when first laid down.

In other words, under certain conditions, cast iron pipe is not durable unless protected. Therefore, it is of importance to the engineer to determine just what those conditions are and how to guard against them.

The salt of the ocean is particularly destructive to cast iron, and its action is manifested in a peculiar way, differing materially from ordinary rusting, scaling and pitting.

In contrast to the cast iron cannon removed from the fresh waters of the Delaware River and found free from rust, Major-General Pasley stated that the cannon of the "Royal George," sunk in the ocean for 62 years, and of the "Edgar," submerged for 133 years, had been examined by him. The cast iron had generally become so soft that the metal resembled plumbago in appearance and could be cut with a knife. The cast iron shot became red hot on exposure to air, and fell to pieces, but the cannon hardened after a time.

It is well known that iron filings will burn in the flame of a candle, and that very finely divided iron, obtained by the reduction of its oxides in hydrogen, is pyrophorous, that is to say, it ignites spontaneously on exposure to air. These cannon balls, therefore, may have contained a remnant of metallic iron in an exceedingly fine state of subdivision. The heating may also have been due to the rapid change from ferrous to ferric hydrate on exposure to air, or to a combination of the two causes. Just why the shot should heat up and fall to pieces, when the cannon did not, is difficult to explain.

The corrosive action of sea water is not uniform under all conditions, but may be materially accelerated or retarded. A case of this sort is cited by Mr. Robert Mallet:

> Iron under certain circumstances is subject to a peculiar increase of corrosive action—as, for instance, cast iron piling at the mouth of tidal rivers. The salt water being of greater density than the fresh, forms at certain times of tide an under current, while the upper or surface water is fresh; these two strata of different constitution coming in contact with the metal, a voltaic pile of one solid and two fluid elements is formed; one portion of the metal will be in a positive state of electrical action with respect to the other, and the corrosive action on the former portion is augmented.

Cases occur with considerable frequency, where trouble has resulted from laying cast iron mains in saline soils.

In 1902, the Elizabethtown Water Company, Elizabeth, N. J., laid about 2 miles of 6" main across salt meadows. It was ordinary coated water pipe, about 0.45" thick, laid about 8 inches below the surface of a salt marsh. The surface of the marsh was about 18" above ordinary high water, and covered at times by salt water. The nearest trolley is about 3 miles away, so that stray currents had nothing to do with the observed deterioration. Only 7 years after it was laid, the pipe began breaking under pressure of 40 pounds, and it was necessary to renew the whole line in 1912. Internally it was in good condition. The external appearance was equally good, there being no pitting, but on closer examination, sometimes the top, sometimes the bottom, and, at other times the sides, were found to have large spots where the iron appeared to be leached out, so that it could be cut like soft graphite. This action was not regular, sometimes skipping several feet, but was worst on the bottom. In some instances these soft places had eaten completely through, and although not pitted or swelled out, had lost all the characteristics of iron. After exposure to the air, this metamorphosed iron hardened. At Perth Amboy, N. J., similar trouble was experienced. A 16" main, crossing a salt meadow for some 3,500 feet, had to be abandoned in less than 20 years.

At Atlantic City, N. J., the water main leads through salt marsh for a distance of 22,000 feet. In 1882 a 12" cast iron main was laid, which, in 1888, was paralleled by a 20" main, and in 1901 by a 30-inch steel main. In 1911 a 48-inch wood stave main was laid parallel to the three for about 7,000 feet, after which it takes a different route for the remainder of the line. Both the cast iron mains are soft in spots, and blow out from time to time under a pressure of

50 pounds. The deterioration is like that at Elizabeth and Perth Amboy. The steel pipe is even less satisfactory; though laid at a later date, it is rapidly deteriorating, and 6,000 feet of it are now out of service. The top of each of the two cast iron mains is about 1 foot below the surface of the meadow; the steel main is about half its diameter below the surface, the top covered with meadow sod.

At Richmond, Va., about 400 feet of 6″ cast iron pipe, laid in a salt blue marl, in 20 years became soft enough to cut with a knife, the action appearing to be equally great at its top, bottom and sides. A trolley track, 450 feet distant, may possibly have contributed to the disintegration.

Trouble has been experienced also from saline soils at points remote from the ocean. The Bureau of Water of Syracuse, N. Y., has had much trouble from corrosion or disintegration of water pipe in the salt lands. A line of pipe runs in a very low section of these lands, the major part of which is under water a large portion of the year. The part which is continually submerged has not disintegrated, but that adjacent to it, laid about 1904, began to fail after several years' service. The pipe was sound in parts, and at the leaks it could be cut with a knife.

A third soil destructive to cast iron pipe is noted at Syracuse:

> Since submitting this matter to you, I have observed two cases of disintegration in different parts of the town, the pipe being eaten precisely as that in Spring Street. In each case the soil above the pipe was composed in the main of coal ashes, and apparently the constant trickle of water had created some chemical action which ate the pipe. As a layman, I have concluded that coal ashes, where there is a possibility of a flow of water through them, are responsible for this particular kind of disintegration.

In Germany, R. Krzizan cites a case where a portion of an asphaltum-coated cast iron water main that had been in service for 20 years, suddenly became defective. A number of conical holes were scattered irregularly over the surface and were surrounded by graphite-like material containing particles of metallic iron. There was nothing in the water running through the pipe to account for this formation, but crystals of gypsum were distributed irregularly in the clay in which the pipe was laid. Krzizan attributes the corrosion to local currents set up between the graphite particles and the iron, in the presence of a solution of calcium sulphate, at the points where the crystals of gypsum were contained in the clay.

A question arises as to what effect the alkali soils of the West would have on cast iron pipe, and it is hoped that information on this point may be brought out.

The greater part of Montrose, Col., is underlaid by soil having an alkali content of from 200 to 400 parts per 100,000, and portion where it ranges from 600 to 1,000 parts per 100,000.

The superintendent of water supply states that the system, built in 1888, consisted of 4″, 6″ and 8″ wrought iron pipe, which deteriorated so rapidly that it was all replaced either by cast iron or wood stave pipe, except about 800 feet of 8″, which is still in fair condition. Cast iron pipe that has been in use for nearly 20 years appeared to be in excellent preservation, and has never given any trouble. The alkali soil, however, has been disastrous to the wire of the spiral-wound wood stave pipe. It was laid in 1905, and will have to be removed in a few years. There are no trolleys, and the pipe is laid 4 feet below the surface.

Before attempting to draw any conclusions from the facts presented, it will be desirable to consider the composition and character of cast iron, and to review the theory of its corrosion, and study some experimental data bearing on the subject.

The Composition of Cast Iron.—Cast iron is a substance of varied composition, both physically and chemically. It is known that common salt added to water progressively lowers the freezing point until, with 23.5% of salt present, the whole mass freezes at —22° Cent. This is said to be the "eutectic" composition, a compound that has a lower fusing point (or freezing point) than its components. With percentages less than the eutectic, crystals of ice form when the temperature of the water falls, the mother liquor becoming more concentrated, until the eutectic composition is reached, when the whole solidifies.

Pig iron, similarly, may be termed a frozen solution of carbon and iron. If no other impurities were present it would contain 4.3% of carbon, but addition of carbon lowers the solidifying point to the eutectic 1135°, and then raises it again as additional percentages are present. The free graphite found in cast iron, therefore, is due to the same action as the solid plates of salt frozen out of the water, with this important difference, that whereas ice does not retain any salt in solid solution, the solidified iron retains much carbon.

In pig iron heated considerably above its fusing point, the carbon tends to separate in the graphitic form, whereas the same metal heated to a lower degree, on cooling would retain more carbon in the combined condition. Much study has been devoted to this obscure subject, and a series of modifications of iron and iron carbon, all due to different conditions of heating and cooling, have been investigated.

To summarize briefly: The metal in the bottom of a blast furnace is a saturated solution of carbon in iron, and as it cools to the solidifying point, carbide is thrown out of solution. This splits up into iron and carbon. Iron solidifies, the mother liquor splits up, and the same process is repeated. It is analogous to the behavior of the salt solution.

The carbon in a casting, ordinarily 3 to 4%, may be all in the combined state, forming the intensely hard carbide of iron (Fe_3C) with a characteristic white fracture; or it may be in the form of free graphite, the numerous plates of which cut up and weaken the matrix of ferrite, the whole having the fracture of gray iron.

Each added impurity (and many are invariably present) increases the complexity of the casting, both chemically and physically, and sets up innumerable nodes for electrolytic differences of potential.

Corrosion of Cast Iron.—The rusting of iron is by no means the simple process it was once thought to be. How heterogeneous a casting may be in composition and physical structure has been shown. This adds materially to the difficulty, and explains the often apparently discordant results obtained by careful investigators.

Five separate theories have been advanced for the rusting of iron, but three of these have been practically eliminated, leaving two over which the fight still wages; the acid theory and the electrolytic theory. The one undisputed fact is that iron cannot rust in air unless water is present, nor in pure water unless oxygen is present.

The acid theory regards corrosion as resulting from an acid, usually carbonic, which unites with the iron to form ferrous carbonate ($FeCO_3$) for the soluble ferrous hydrogen carbonate ($FeH_2[CO_3]_2$), and the liberated hydrogen combines with any dissolved oxygen in the water to yield water. The oxygen of the air next converts the soluble iron salt into hydrated oxide, or rust, liberating the carbon dioxide (CO_2) which is now free to attack a fresh portion of iron. With a supply of water and oxygen, a small portion of carbon dioxide could thus rust an indefinite quantity of iron.

The electrolytic theory holds that the presence of an acid is not necessary, regarding the action as electrochemical.

If two platinum plates are immersed in a solution of common salt ($NaCl$), one plate connected to the positive and the other to the negative pole of a battery, hydrogen will be given off at the negative plate and oxygen at the positive. If a few drops of a solution of litmus are added, the liquid around the positive plate shows red, indicating the presence of an acid, and around the negative pole turns blue, showing alkali. The appearance of gases, and of red and blue color, is noted at once when the battery wires are connected, even if the plates are separated by quite a quantity of solution, giving strong support to the supposition that matter travels with the current, part toward the positive and part toward the negative pole.

If steel is immersed in a solution of copper sulphate ($CuSO_4$), iron dissolves and copper is deposited, the electric charge being transferred from the ions of copper to those of iron. Electrochemically, hydrogen is a metal classed with copper in relation to iron. If, therefore, iron is placed in a solution containing hydrogen ions, a similar reaction will take place, iron being dissolved and hydrogen passing from the electrically charged or ionic state to the atomic or gaseous condition, and is deposited on the iron. Ferrous salts, as well as ferrous hydroxide, are rapidly oxidized to the ferric state, if air or oxygen is present.

It is a matter of common observation that iron rusts in patches or spots. It has been noticed that if rusting takes place in water or in a neutral solution of an electrolyte, such as salt, to which a little phenol phthalein had been added, a pink color developed and is confined to certain nodes or spots. This pink color is a proof of the presence of hydroxyl ions, and indicates the negative poles. Add a trace of potassium ferricyanide to the solution and if iron goes into solution, ferrous ions must appear, which, with the ferricyanide, form Turnbull's blue. This reagent indicates at once the positive and negative poles.

Whatever may be facts concerning the electrolytic and acid theories, if absolutely pure iron, pure oxygen and pure water are used, both reactions take place under actual conditions of corrosion.

Natural waters are usually charged with dissolved oxygen and carbon dioxide from the air, thus readily permitting the action of carbonic acid on the iron. Even the purest commercial wrought irons are not homogenous, either physically or chemically, so that electrolytic action also comes into play.

It is a noticeable fact that in most cases of bad pipe corrosion that have come to the writer's notice, not only was there salt water, aeration, and more or less motion in the water, but the pipes were laid, as a rule, in muck with rank swamp vegetation in contact with the metal. The action of living matter, therefore, becomes of interest and merits careful consideration.

The direct action of any organism is doubtful, although it is known that organisms do occur in the tubercles forming on the inside of water mains. Dr. Brown states that "Organisms are found in some incrustations and may modify their composition; on the other hand, incrustations are often free from every trace of life." Mr. Richard Gaines found it probable that certain sulphur bacteria were responsible, in part at least, for rust tubercles and pitting in conduits; and cites that during repairs to the foundations of a bridge across Lake Hauser, Montana, the workmen found protuberances they called "shell rust" scattered over the surface of submerged steelwork. Schorler identified in this rust *Gallionella ferruginea* in large quantities. Apparently the iron is dissolved by some acid secretion from these organisms, and, in this instance, the structural damage to the bridge had been enormous. It is even necessary to consider the earthworm. It has been estimated that some 25,000 worms exist in every acre of soil, and each worm annually ejects 20 ounces of soil as castings, which means that 15 tons of soil in every acre of land pass through the worms each year. These castings are acid when fresh, and contain also small quantities of ammonia. With 15 tons of acidified soil per annum, with a small admixture of ammonium salts, there may well be a corrosive action on embedded iron.

Of still greater importance is the action of plants:

> Young roots, and especially root hairs, in addition to exhaling carbonic acid, excrete stronger acids, or acid salts, by means of which they dissolve insoluble bodies. That this is the case is readily demonstrated by allowing the roots to grow upon a polished plate of marble, when the latter will be corroded with an etched pattern showing the path of the roots. By placing the roots upon paper dyed with litmus their acidity may ready be demonstrated. Furthermore, when plants decay, humus acids result which are powerful solvents.

How important these acids may become is illustrated by some recent experiences in Illinois:

In Southern Illinois a peculiar condition exists which undoubtedly has a material bearing on the corrosion of steel structures. In that portion of the state popularly known as Egypt, a large proportion of the surface soil shows a marked acid reaction. This condition exists generally throughout the greater part of the state that lies south and east of the Kaskaskia River and south of the latitude of Mattoon. To a less marked degree, the soil is acid in many places elsewhere in the state, where land has been farmed for 50 years or more.

This acid condition does not exist for a depth of more than a few inches, and steel buried at a greater depth does not seem to exhibit any unusual tendency to corrode.

The destructive effect of carbonic acid has already been referred to; in swampy waters, for the reasons mentioned. it is high, and also in many well waters. It is, moreover, very soluble in water, so that it is in available form to attack any iron exposed to its influence.

It can be readily understood, therefore, that, by their secretions, plants and animals are important accessories in the corrosion of iron.

Conditions Inhibiting Corrosion.—While dilute solutions of alkalis do not retard corrosion, strong solutions neutralize the acids and preserve iron. For instance, 5% of lime applied to boggy, sour land exerted a pronounced retarding action on the corrosion of ironwork embedded in it. The same authority further says:

> There should be many cases where the property of alkalis to inhibit corrosion could be made of more practical use than has been done. Whenever iron posts or standards are set directly in the ground, the liberal use of slaked lime should be beneficial. The effect of concrete in protecting iron and steel is because of the two or more electrolytes in one solution.

Cast iron is poured into sand moulds, and the outer skin, therefore, is silicious. A 20% alloy of iron and silicon is not attacked by acids, and is virtually uncorrodible. Wallace refers to iron forged on a stone anvil, which does not rust on exposure to the weather, but takes on a fine brown patina. The question was raised whether the stone anvil did not siliconize the skin of the iron. By experiments it was found that, under a given length of exposure in soil, if the corrosion of machined cast iron was considered as 100, that of cast iron retaining the original surface was only 93.

This table, from various published data, shows the protective effect of the skin.

RELATIVE CORROSION OF CAST IRON WITH AND WITHOUT SKIN.

	Foul sea water.	Clear sea water.	Foul river water.	Pure air and clear river water.	City air or sea air.
Cast iron ..	3.500	3.386	2.034	0.604	2.637
Cast iron (skin removed by planing) .	12.275	4.738	3.884	0.584	4.763

Silicon is an undesirable alloy for iron in many ways, so that surface treatment, such as occurs in casting, is probably the only method of making use of its rust-inhibiting properties.

Chromium, nickel and copper, in small quantities, contribute greatly to the resistance of iron to corrosion. A steel containing about 1% of chromium was found by Hadfield to corrode about half as much as ordinary mild steel. Similarly, 3% of nickel added to steel reduced its relative corrosion in salt water about 50%. Phosphorus in iron also retards corrosion; differing in this respect from sulphur, which, by forming sulphuric acid, powerfully attacks the metal.

The coating of iron with zinc and tin is also used to inhibit corrosion. Zinc is electro-positive to iron, and if the two metals, in contact, are emerged in a corroding solution, the zinc will pass into solution and the iron remain unaffected. Galvanizing, therefore, is not merely a mechanical shield to the iron, but protects the metal for some distance around it. It is well to emphasize this fact, as it is a point frequently misunderstood. Tin, on the contrary, is not electro positive to iron. Being itself practically unaffected by corrosion, it protects the iron mechanically. The tin coating, as commercially applied, is full of minute pin holes, and does not inhibit corrosion at these points, thereby differing from zinc.

TYPICAL CASES OF DETERIORATION OF CAST IRON PIPE.

With these various facts in mind, an examination of typical cases of pipe failure may give information of value.

It has already been noted that most, if not all, pipe failures occur from the influence of salt or saline waters.

A 10″ main runs southward from Elizabeth, N. J., through the meadows to Morse's Creek, and is continued by a 6″ line. The general elevation of the meadow is about 18 inches above mean high tide, and the bottom of the pipe is approximately at the high tide level. There is no trolley near. Curiously enough, the 10″ pipe, laid in 1893, has shown no appreciable deterioration except at a point opposite the works of the Standard Oil Company, where escaping acid waters caused corrosion. The 6″ line, although not laid until 1902, has broken down completely. Both sizes were made by one company, and there is no apparent reason for the greater resisting power of the 10″ line.

The marsh is intersected by creeks and ditches, and the surface largely covered with fox grass. The patches too wet for the fox grass are covered with what is known as quill sage, a coarse, rank swamp growth, and it is in these that the chief damage to the pipe occurs.

The corroded portion has the general appearance and consistency and cuts like graphite. When first removed from the swamp it is softer, more like putty. When it is pulverized for analysis it is brown, and makes a brown streak on paper.

Filings from the corroded part, if sifted on a card with magnet beneath, fall as an inert mass, showing that when carried to completion, the iron is completely changed from the metallic state.

One piece of the corroded portion had this composition:

CORRODED PORTION OF PIPE FROM ELIZABETH.

Iron	50.62 per cent
Silica	0.31 per cent
Chlorine	0.72 per cent
Maganese	0.46 per cent
Silicon	22.32 per cent
Combined carbon	0.63 per cent
Graphitic carbon	5.51 per cent

At a part not very deeply corroded, the specific gravity of a complete cross-section of the pipe was 5.18, and a piece from the corroded part of the pipe was only 2.2. The specific gravity of cast iron is assumed to be 7.15.

At Atlantic City the behavior of the pipe was similar to that at Elizabeth. The conditions also were analagous, the chief difference being that the salt meadow was only 6 inches above mean high tide, so that the pipe was subjected to more frequent alternations of water and moist air.

Two samples of soil were collected from the Atlantic City meadows, one of them ½″ from a corroded cast iron main and the other 3 feet away. The analysis is given below:

ANALYSIS OF SOIL FROM ATLANTIC CITY MEADOWS.

	Soil within ½ in. of pipe. %	Soil away from pipe. %
SiO_2 (insol. in HCl)	18.68	32.27
Al_2O_3, CaO, etc.	10.57	22.78
SiO_2 (sol. in HCl)	0.23	0.28
Al_2O_3 (sol. in HCl)	1.91	1.19
Fe_2O_3 (sol. in HCl)	46.57	9.11
NaCl	1.93	0.95
CaO (sol. in HCl)	0.99	0.83
MgO (sol. in HCl)	0.00	0.00
Sulphates	0.00	0.00
Organic acids	0.00	0.00
H_2O (at 105° cent.)	6.28	28.92
Volatile matter besides H_2O (ignition)	13.27	3.96

It has been shown that aqueous solutions of most acids dissolve iron. If hydrochloric acid is used, ferrous chloride and hydrogen are the resultant products, the former oxiding into ferric chloride in the presence of air. It has also been shown that if only a trace of acid is present, the iron will be deposited from the solution as hydrated ferric oxide. It is probable that in salt water the reaction may be represented by the equation:

$$Fe + 2NaCl + 2H_2O = FeCl_2 + 2NaOH + H_2.$$

In the presence of air, or of dissolved oxygen in the water, the free hydrogen oxidizes to water, the iron in solution yields ferric hydroxide, and the process continues. The chemical analysis of the portion practically free from metallic iron contains as low as 42.2% of that element, a small part of which is in the form of chloride. Clearly, part of the iron has been removed in solution and part remains as the hydroxide, the carbon present in the combined form being left behind, and, as shown in the microscopic sections, has thickened the plates of free carbon originally in the free iron.

The chlorides of sodium and potassium cannot corrode iron in the absence of air. Magnesium chloride, which is present in sea water in small quantities, is able to do so, but to get the full corrosive effect of sea water, plenty of air is essential.

It has been shown that the greater the surface of liquid exposed to the air, the more the corrosion is intensified.

In the salt marshes in question, the tide rises and falls, passing through a multitude of creeks and ditches all over the meadows. At Elizabeth, it ordinarily reaches about to the bottom of the pipe; at Atlantic City, it covers it, affording ideal conditions for corrosion. The liquid at high tide touches or surrounds the pipe; at low tide it falls, air rushes in to take its place, and a moist, saline, oxygenated, spongy mass of earth and roots surrounds the pipe. Carbonic acid probably contributes to the action. The Atlantic City meadow soil was free from organic acids. In the sample of soil taken ½-inch from the pipe, there was 46.57% of Fe_2O_3 and even 3 feet away iron occurred in large quantities, there being 9.11% of Fe_2O_3. This would appear to show that it had been dissolved from the pipe as $FeCl_2$, and, after diffusing or flowing away from the pipe as the tides rose and fell, was deposited as hydroxide.

It is to be noted that at Elizabeth, where the top of the pipe was not so frequently wet as the bottom, the blow-outs generally were in the bottom of the pipe. At Perth Amboy the top and upper sides suffered most. At Atlantic City, also, the condition was worse at the top than at the bottom. This was to be anticipated on account of the relative elevations of the pipe and high tide. At Elizabeth the high tide reached the bottom of the main; consequently the top was not subjected to the saline influences so frequently. At Atlantic City the pipes were covered at high tide, and, being laid farther below the surface, air was more plentiful at the top, which, therefore, in presence of an ample quantity of salt water, and with a more abundant supply of oxygen than the bottom, suffered most.

At Syracuse, the portions constantly submerged did not give out. Probably, too, the concentrated saline content in these brine-soaked lands produced an inhibiting effect. The damage took place above the permanent water table, where both air and salt water could reach the pipe.

Analyses of the corroded and uncorroded portions of the Syracuse pipe are given below:

ANALYSES OF CORRODED PIPE FROM SYRACUSE, N. Y.

	Non-corroded portion. %	Corroded portion. %
Silicon	0.15	1.49
Sulphur	0.11	0.20
Phosphorus	1.26	1.39
Manganese	0.30	0.38
Total carbon	3.65	4.21
Graphitic carbon	2.85	3.84

"The corrosion contained 33% of insoluble residue, consisting of about 10% graphitic carbon and 22% of silicon (Si) and silica (SiO_2). Total carbon in the corrosion = 11.2%, consisting almost entirely of graphitic carbon. Sulphur in corrosion = 3.0%. Apparently the process which accounts for the corrosion either dissolves the greater part of the combined carbon or converts it into the graphitic variety."

An analysis of the soil surrounding this pipe disclosed that it was acid to phenol-phthalein, and contained 3.42% of organic acids. This is very interesting from its analogy to the soil conditions in Illinois, where steel bridges were damaged so badly by the acid soil.

On the whole, the evidence chiefly observed with cast iron pipe would seem to indicate that organisms, whether animal or vegetable, had but little to do with the effects observed. Salt water and air seem to be the active agents, probably aided by carbonic acid; and the exclusion of either is followed by increased durability of the pipe.

The evidence given where cinders caused pipe corrosion, the similar experience at Syracuse, and the German case resulting presumably from local electrolysis due to the presence of gypsum crystals, indicate the necessity for caution where pipe is likely to be subjected to such influences. Some years ago a tunnel leading from the Susquehanna River to the power house of the Central Pennsylvania Traction Company at Harrisburg, was constructed through the property of the Central Iron Works, on parts of which there were large slag dumps. The water flowing into the tunnel was so sulphurous from the slag that it greatly impeded the work, and was unwholesome for the workmen. Cast iron pipe in such a location would undoubtedly undergo rapid deterioration.

Where low lands are filled with cinders, ordinarily no trouble need be feared, but when subjected to periodical wetting and aeration, some precautions are desirable.

Acid mine waters are also very corrosive, and should be guarded against. In the mines themselves this would generally be economically impracticable, but in municipal works in the vicinity, where the pipe may be attacked, preventive means should be resorted to.

Prevention of External Corrosion.—Bearing in mind the silicious skin of cast iron pipe and its protective effect, and noting that chromium alloys of iron are resistant to acid attack, it occurs to the writer that some chromium compound, such as chromite, mixed with the facing sand of the moulds might produce in castings a protective chromium skin.

It is a subject wherein an apparently well-reasoned argument may be completely upset. For example, as zinc in water, either fresh or salt, protects iron and is itself attacked, so if iron and copper are immersed in a liquid capable of acting on each, and connected by a conductor, a current will pass from the copper to the iron, and the iron will be dissolved. And yet, after a series of exhaustive experiments, Mr. Richard H. Gaines states:

"The legitimate conclusion from the foregoing experiments is, that rather less than more galvanic action arises from contact between steel and the other metals of the series, than from contact between steel and steel. In actual practice it has been found that if a steel nut is put on a steel bolt and subjected to corrosive conditions, in a comparatively short time the steel nut will have to be split off, if gotten off at all, on account of rusting together; whereas a brass or bronze nut on a steel bolt under similar conditions can be readily screwed off."

Mr. H. J. Force is authority for the statement that cast iron in pumping machinery was badly corroded by acid mine waters and as bronze bushings, valves, and impeller blades were used, it was thought that the action was due to galvanic action from contact of the two metals in the acid water. On substituting cast iron for the bronze valves and bushings so that the parts in contact would be of the same metal, the corrosion increased, and the cast iron deteriorated even more rapidly than when in contact with bronze. As far back as A. D. 79, this effect of iron on iron was noted. Pliny states that Alexander the Great, to repair a bridge over the Euphrates, "sometime bound and strengthened the bridge over there; the links whereof, as many as have been repaired and made new since, do gather rust, whereas the rest of the first making be all free therefrom." Modern experience has shown that if the old and new iron are of absolutely similar metal, one will be as durable as the other; but that if they are of a slightly different composition, it is not necessarily either the inferior or the newest metal which suffers most, that depending on the electrical phenomena resulting.

It is unsafe to reason too positively from results obtained with liquid electrolytes, as to what will happen to iron buried in soils. Moreover, time is such an important factor that conclusions drawn from accelerated tests may be most misleading.

"The relatively high rate of self-corrosion of cast iron as compared to the other kinds of iron tested is contrary to the generally accepted idea that cast iron is more resistant to self-corrosion than wrought iron. It is not improbable that this impression in regard to the superiority of cast iron has grown out of the fact that cast iron structures are usually made relatively heavy, and they tend to corrode more uniformly than wrought iron or steel, both of which factors would tend greatly to increase the life of the former."

The writer cannot subscribe to this view. The ordinarily accepted idea of the superior durability of cast iron arises, in his opinion, from the fact that cast iron, generally speaking, is more durable than commercial forms of wrought iron and steel.

A second method of protecting cast pipe, based on the rust-inhibiting properties of the chromates and certain other substances, whereby the iron is rendered "passive," does not seem practicable, in that a sufficient quantity of material to protect the iron indefinitely could scarcely be added to the soil surrounding the buried pipe at a reasonable cost. Therefore, this interesting phase of the subject has not been taken up in this paper.

The use of lime in the trenches, so as to encase the pipe in an inhibiting alkali, ought to be of service, and is worth trying. Encasing in concrete would be expensive, but would protect the pipe if properly done.

Another method, suggested at Perth Amboy, is to leave the pipe in open trench. This might help materially, as the alternate wetting and drying would probably be less destructive than the constant exposure to moist air, salt, and carbonic acid in the swamp or meadow soil. At Atlantic City this principle has been carried one step further, and the new 48-inch cast-iron water main across the salt marsh has been raised above the surface of the meadow about a foot so as to be entirely in the air. This would seem to solve the problem in a warm climate, or where the main is large enough to be exposed without danger of freezing, and where it is permissible to have the pipe above the service.

Bearing in mind the protective effect of zinc, it might at times be desirable to galvanize the cast iron in such locations, instead of giving it the ordinary bituminous coating. The United States Government has utilized galvanizing in some instances for the protection of gratings, covers, and similar castings; but as far as the writer is aware, it has never been applied to cast-iron pipe. Double galvanizing, as it is called, should be used in such cases. This is a trade term, which does not mean that the iron has been dipped twice, but merely that it carries a much heavier coating.

CONCLUSIONS.

First.—Under ordinary conditions of soil, cast-iron pipe has a probable life of from one to three centuries, as far as external corrosion is concerned.

Second.—Under certain soil conditions, such as salt marshes or saline soils, cast-iron pipe may be rendered useless in from 7 to 20 years.

Third.—At times, cinder and slag fills may exert a strongly deleterious influence. Acid mine waters are also destructive.

Fourth.—Substituting wrought-iron or steel pipe for cast iron is ineffectual. Cast iron will outlast the others.

Fifth.—Remedies fall under four heads:

A—Increasing the skin resistance of cast iron;

B—Utilizing the protective influence of alkalies by surrounding the pipe with lime or cement, where such is practicable;

C—Exclusion of acids, salt, or air;

D—Galvanizing the cast-iron pipe, thus protecting it at the expense of the zinc.

Sixth.—So many opposing factors are at work simultaneously that great caution is necessary in reasoning from effect to cause, and in suggesting remedies based on observed facts. The unexpected frequently happens.

The Testing of Rubber Goods.

The Bureau of Standards, Department of Commerce, is about to issue the third edition of a circular on the testing of rubber goods, which will be free on application. This publication, which has been very much enlarged, is fully illustrated and describes in detail the method of procedure in conducting physical and chemical tests of rubber. The testing machines and apparatus developed at the Bureau of Standards greatly facilitate the testing of rubber, and the object of this circular is to assist manufacturers and consumers in establishing standard specifications and standard methods of test. The subject matter proper is introduced by a brief outline of the processes through which rubber passes before reaching the factory, followed by a short description of the usual processes of manufacture, which include washing, drying, compounding, "making-up" various articles, and vulcanizing. The physical tests most commonly employed are explained very thoroughly. These include tests for tensile strength, ultimate elongation, and elasticity. Conditions affecting the results of tests are discussed at some length, and experimental data are given to show the necessity of a standard procedure in testing. A general discussion of the chemistry of rubber is followed by a brief explanation of the object of each of the analytical determinations that are commonly made. After this there are given in detail the methods in use at the Bureau of each of these determinations. They are not entirely original, but have been compiled from the various publications on rubber analysis, from the information gained through the routine testing of rubber goods for delivery on Government contracts, and from co-operative research with various scientific organizations. The tentative method of analysis and specification for 30 per cent Hevea insulation compounds, adopted by the joint Rubber Insulation Committee, and next given. A bibliography listing the more important books and journals devoted to rubber and the Bureau's regulations regarding the testing of rubber goods conclude the circular.

METALLURGY

FATIGUE OF COPPER ALLOYS.*

By ERNST JONSON.

SUMMARY.

Experience has shown that copper alloys are subject to cracking under certain conditions of stress and exposure. In order to determine the magnitude of the stress at which cracking is liable to occur, a series of long-time tension tests has been started, in which the test specimens are exposed to the action of ammonia while under stress. In order to discover which alloys are subject to cracking, all the common alloys will be included in this series of tests.

Results have been obtained from the following alloys: Manganese bronze, naval brass, Muntz metal and gun metal. All the specimens of these metals cracked when the stress reached a value between 20,000 and 27,000 lbs. per sq. in. Specimens of manganese bronze exposed to high stresses for a long time, but protected from corrosion, did not crack. Other specimens of manganese bronze, which were corroded without being under stress, were not injured thereby.

The following conclusions have been drawn from the tests:

Excessive stress alone does not injure copper alloys, nor does corrosion alone, or corrosion accompanied by moderate stress. Corrosion, accompanied by prolonged stress exceeding 20,000 lbs. per sq. in. is liable to cause cracking in any of the above-mentioned alloys. We must therefore regard 20,000 lbs. per sq. in. as the practical ultimate strength of copper alloys, and the working stress must be taken as a safe fraction of this ultimate strength.

In previous papers[1] the writer has pointed out that the occurrence of so-called season cracking in brass rods is conditioned by (1) high initial tensile stress in the surface of the rod, and (2) by corrosion of the metal; also, that a brass rod may develop cracks of the same nature as season cracks when stressed beyond the initial yield point by an external load, instead of having initial stress set up by the cold drawing of the rod, and that such cracking is not peculiar to one kind of brass but that all kinds of forgible brass are subject to it.

At the time of the previous writing, the following brasses were tested and cracked when etched with ammonia, while under stress greater than the initial yield point: Cast manganese bronze from two foundries, plain-extruded manganese bronze, rolled and-drawn manganese bronze, plain-extruded naval brass, drawn naval brass, and plain-extruded Muntz metal. No cracking has been observed where high stress and corrosion did not co-exist. From these facts the conclusion was drawn that the ordinary ultimate strength of brass is developed only when the metal is broken so quickly that cracks do not have time to develop, and that when a stress exceeding the yield point is applied for a considerable time the metal will fail by cracking.

The working hypothesis formed for the purpose of co-ordinating these facts and to guide further investigations is as follows:

In copper alloys there are microscopic flaws. When the tensile stress approaches the yield point these flaws are opened sufficiently to admit corrosion. This corrosion weakens the edges of the flaws and causes them to increase under the continued action of the stress, and thus a continuous crack is formed which gradually increases in depth. When the crack has so reduced the cross-section that the stress on the remaining solid portion exceeds the ultimate strength, the rod breaks.

In order to more definitely determine the magnitude of the stress at which cracking begins another series of tests has been started. Each test was made as follows: A tension test specimen of 1 in. diameter and 8 in. length, with a reduced diameter of 0.8 in. and 6-in. gage length, was placed in the testing machine. A sheet steel cup with a 1-in. hole in its bottom was put on top of the lower grip so that the end of the test specimen passed through it, and the cup was filled with strong ammonia. Some absorbent cotton was tied to the test specimen so as to keep it wet by capillarity, and the cup and test specimen were covered by a conical paper hood so as to confine the ammonia fumes. A stress of 10,000 to 17,000 lbs. per sq. in., increased in increments of about 3,000 lbs. per sq. in. at intervals of a day or more, was applied to the test specimen. Under the higher stresses the test specimen continued to stretch for a considerable length of time, and in such cases this time was added to the interval between the additions of load.

The test specimen was examined before each increment of load was applied. When the first crack was seen the test was concluded, because experience has shown that a crack once started will increase in extent until the test specimen fails, even if the load is not increased. The cracks were similar to season cracks; the largest was generally found where the test specimen emerged from the liquid. In some cases this crack was the only one present; in others there were quite a number of cracks distributed over the length of the test specimen.

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*Paper presented before the 18th annual meeting of the American Society for Testing Materials.

[1] "Cracking of Drawn Brass," Engineering Record, April 11, 1914; "Troubles Experienced with Forgible Brass during the Construction of the Catskill Aqueduct," Proceedings, Am. Inst. Metals (1914).

TABLE 1.—RESULTS OF TESTS (Continued).

Time of test.	Load, lb.	Stress, lb. per sq. in.
TABLE I.—RESULTS OF TESTS.		
No. 1—Manganese Bronze, Plain Extruded		
Time of test.	Load, lb.	Stress, lb. per sq. in.
Nov. 23, 1914, 10:40 a. m., to 25, 10:40 a. m.	5,000	10,000
Nov. 25, 10:40 a. m., to 27, 10:40 a. m.	6,500	13,000
Nov. 28, 11:30 a. m., to 30, 10:15 a. m.	10,000	20,000
Nov. 28, 12 noon, beam had dropped 0.5 in. and was raised.		
Nov. 30, 5 p. m., to Dec. 3, 10 a. m.	11,500	23,000
Beam had to be raised every half hour until Dec. 5, 11:30 a. m.		
Dec. 5, 10 a. m., to 7, 10 a. m.	11,500	23,000
Dec. 7, 1 p. m. to 1:30 p. m.	13,500	27,000
Beam dropped and was raised continually until specimen broke by cracking. There were numerous cracks in immersed portion of test specimen. The last increment of load was evidently too great. A smaller increment probably would have started cracking.		
No. 2.—Manganese Bronze, Plain Extruded, Heated to Near Melting Point, Quenched in Water.		
Dec. 18, 9 a. m., to 19, 9 a. m.	7,000	14,000
Dec. 19, 9 a. m., to 20, 9 a. m.	8,500	17,000
Dec. 20, 9 a. m., to 21, 9 a. m.	10,000	20,000
Dec. 21, 9 a. m., to 24, 5 p. m.	11,500	23,000
Beam raised continually.		
Dec. 24, 5 p. m. The specimen failed by cracking; two large cracks on opposite sides of specimen, each crack extending over half circumference; two minor cracks; all in immersed portion. See Fig. 1(*a*).		
No. 3—Manganese Bronze, Plain Extruded.		
Dec. 24, 9 a. m., to 28, 9 a. m.	8,500	17,000
Dec. 28, 9 a. m., to 29, 9 a. m.	10,000	20,000
Dec. 29, 9 a. m., to 30, 12 m.	11,500	23,000
Dec. 30. Beam dropped and was raised continually. Specimen failed by cracking; one large and several small cracks in immersed portion.		
No. 4—Naval Brass, Plain Extruded.		
Mar. 25, 1915, 3:30 p. m., to 26, 3:30 p. m.	5,000	10,000
Mar. 26, 3:30 p. m., to 29, 12 m.	6,500	13,000
Beam raised Mar. 27, 9 a. m., and 28, 9 a. m.		
Mar. 29, 12 m., to Apr. 1, 1 p. m.	8,500	17,000
Beam raised Mar. 29, 1 p. m., 3:30 p. m.; Mar. 30, 9 a. m., 1 p. m.; Mar. 31, 9 a. m., 1 p. m. Specimen removed from machine Apr. 1, 1 p. m. to 3 p. m.		
Apr. 1, 3 p. m., to 2, 12 m.	10,000	20,000
Beam raised Apr. 1, 5 p. m.; 2, 9 a. m. and 10 a. m.		
Specimen failed by cracking, at 12 m., Apr. 2. Three large cracks, and some minor ones in immersed portion. See Fig. 1(*b*).		
No 5—Muntz Metal, Plain Extruded.		
Mar. 8, 1 p. m., to 9, 3 p. m.	5,000	10,000
Mar. 9, 3 p. m., to 10, 3 p. m.	6,500	13,000
Mar. 10, 3 p. m., to 15, 5 p. m.	8,500	17,000
Beam raised Mar. 10, 5 p. m.; 11, 9 a. m., 11 a. m., 1 p. m., 5 p. m.; 12, 5 p. m.; 13, 5 p. m.		
Mar. 15, 5 p. m., to 24, 5 p. m.	10,000	20,000
Beam had to be raised continually from Mar. 16, 9 a. m., to 22, 3 p. m.		
Mar. 24, 5 p. m., to 25, 3 p. m.	11,500	23,000
Beam raised continually until 3 p. m. on Mar. 25, when specimen failed by cracking. One crack appeared near the upper thread and one near the lower thread. Several other cracks appeared on the immersed portion.		
No. 6—Gun Metal (88 Cu, 10 Sn, 2 Zn) Cast.		
Apr. 2, 1 p. m., to 5, 9 a. m.	5,000	10,000
Beam raised Apr. 3, 9 a. m.		
Apr. 5, 9 a. m., to 8, 9 a. m.	6,500	13,000
Beam raised Apr. 5, 12 m., 5 p. m.; 6, 9 a. m.		
Apr. 8, 9 a. m., to 14, 12 m.	8,500	17,000
Beam raised Apr. 8, 10 a. m., 11 a. m., 12 m., 2 p. m., 5 p. m.; 9, 9 a. m.; 10, 9 a. m.; 12, 9 a. m.; 13, 9 a. m.		
Apr. 14, 12 m., to 20, 9 a. m.	10,000	20,000
Beam raised continually until Apr. 15; then Apr. 15, 9 a. m., 11 a. m., 3 p. m., 5 p. m.; 16, 9 a. m., 3 p. m., 5 p. m.; 17, 9 a. m.; 18, 9:30 a. m.; 19, 9 a. m.		
Apr. 20, 9 a. m., to 22, 12 m.	11,500	23,000
Beam raised continually until failure occurred on Apr. 22, 12 m., by cracking. Crack near top.		

In order to discover what alloys are subject to failure by cracking all the usual copper alloys will be tested.

The stresses at cracking are as follows:

Kind of metal.	Stress at cracking, lb. per sq. in.
No. 1—Manganese bronze, plain extruded	27,000
No. 2—Manganese bronze, plain extruded	23,000
No. 3—Manganese bronze, plain extended	23,000
No. 4—Naval brass, plain extruded	20,000
No. 5—Muntz metal, plain extruded	23,000
No. 6—Gun metal, cast 88 Cu, 10 Sn, 2 Zn	23,000

It appears that the stress at which cracking occurs bears some relation to the elastic limit. but this relation has not yet been definitely established. Present results indicate that the metal is liable to cracking when the stress exceeds the elastic limit by 5,000 lbs. per sq. in.

A detail report on the tests made is given in Table I.

Four specimens of manganese bronze have been under excessive stress for many months but have been protected from corrosion. These specimens have not cracked. Some manganese-bronze studs which were found cracked in valves in the Catskill Aqueduct were made up with red lead. One test bolt, therefore, was embedded in red-lead paste and drawn up to a stress in excess of the initial yield point. In the part of the bolt where the red lead remained liquid, the surface of the metal was stained and cracks appeared.

Two specimens of plain-extruded manganese bronze were corroded, one in ammonia, the other in a mixture of ferric chloride and hydrochloric acid, and then broken in the testing machine. The specimens gave ultimate strengths of 65,300 and 60,000 lbs. per sq. in., and elongations of 43 and 42 per cent, respectively. These results, which are quite normal, indicate that corrosion does not generally injure brass when it is not under stress while being corroded.

The results thus far obtained may be summed up as follows:

1. Prolonged excessive stress does not injure the metal when it is protected from corrosion while under stress.

2. Corrosion does not generally injure the metal when not accompanied by excessive stress.

3. Corrosion accompanied by prolonged stress less than 20,000 lbs. per sq. in. does not generally injure the metal.

4. Corrosion by ammonia accompanied by a prolonged stress of 20,000 lbs. per sq. in. or more causes cracking similar to season cracking.

5. The foregoing results apply to manganese bronze, naval brass, Muntz metal and gun metal.

6. No copper alloy has as yet been found to which these results do not apply. It is possible, however, that such exceptions exist, either on account of higher elastic limit or greater resistance to corrosion.

CONCLUSION.

Practical experience with season cracking indicates that ammonia is not the only corrosive agent which causes cracking in overstressed copper alloys, but that the corrosion which results from the common conditions of exposure also produces cracking. Ammonia, therefore, may be regarded as a representative corrosive agent, although it attacks these alloys more quickly than the average exposure. The test with ammonia may be regarded as an accelerated test which in a few hours produces results which ordinarily would require days, weeks or months to develop, but which do not differ in kind from the results of the more common forms of exposure. Since all copper alloys in practical use are exposed to various corrosive agents it is probable that sooner or later all metal in use will be affected by corrosion, just as much as the test specimens in the tests here reported. Therefore, it follows that the results obtained from these tests may be expected wherever copper alloys are permanently stressed over 20,000 lbs. per sq. in.

It seems, therefore, that we are justified in drawing the conclusion that forgeable brass and gun metal, and probably copper alloys in general, should never be stressed in practice to 20,000 lbs. per sq. in. In other words, 20,000 lbs. per sq. in. should be regarded as the practical ultimate strength of this group of materials. The working stress should therefore be taken as a safe fraction of this stress, say 5,00 lbs. per sq. in.

An important corollary of this conclusion is that the process of manufacturing rods of copper alloys must be so planned that no appreciable initial tensile stress is left in the surface of the rod, and that the proper inspection of drawn rods must include strain measurements.[2] Another important corollary is that copper alloys cannot be depended on where the stress is indeterminate, for in such cases it may or may not exceed the safe stress. These alloys, therefore, should not be used for important bolts when there is the least occasion for drawing them up very tight.

The total exports of sugar from Java during 1913 amounted to 1,607,265 short tons, as follows: High grades, 1,350,390; in bags, 42,843; inferior grades, 3,374; molasses sugar, 210.658. No sugar was reported shipped to the United States and only 55 tons to the Philippines. The total area under sugar cultivation in Java at the close of 1913 was 359,224 acres.

BRINELL HARDNESS TESTING OF NON-FERROUS ALLOYS.*

By V. SKILLMAN.

Among the more important physical tests to which non-ferrous alloys are submitted there is one which, until recently, has received comparatively little commercial application. Although the hardness of a metal is often of considerable importance to both the manufacturer and engineer, it usually is classified by stating that it is hard or soft without reference to any definite method of measuring that quality. Naturally, the result depends largely upon the personal view of the observer. If the machinist classifies an alloy as hard, the engineer will quite likely find its resistance to compression or indentation is not such as would lead him to call it hard.

Considerable of the confusion is the result of the difficulty in defining hardness. It seems at present impossible to use any scientific unit to express hardness and quite different meanings are embraced by the one general term. As the result of such a condition the methods devised for measuring hardness have been the outgrowths of attempts to obtain data with some particular idea in view in each case. The numerals found are, therefore, empirical and depend upon the method used in their determination.

One of the oldest methods of determining hardness is to ascertain the amount of resistance to stretching. This is the method of the mineralogists. Means have also been devised for its application to metals. Other methods measure the compressive hardness by determining the resistance offered to indentation by another body. A measurement of the elasticity is made use of in some methods, while in others toughness and abrasive qualities are brought into prominence in determining the cutting hardness.

Of the many methods developed, several have lately come into prominence on account of the possibility of their commercial application. One of these used extensively is that devised by Brinell. It is dependent upon the resistance offered by the sample to indentation. The test consists of pressing a hardened steel ball into the surface of the sample being investigated, by means of a definite load and measuring the diameter of the resulting indentation. The hardness numeral is the ratio of the pressure on the sphere to the area of the spherical indentation.

The test can be made in any form of apparatus capable of pressing the ball upon the surface of the metal and measuring the pressure exerted. In the absence of a special piece of apparatus the test may be made with considerable accuracy in the average small size tension-compression testing machine. The machine is arranged as for a compression test, and the steel ball is fastened to the under side of the pulling head as near the center as possible. It is better if it is not fastened to hardened steel, as it will more readily form a seat for itself when making the first impression. No elaborate device is necessary to hold the ball if the specimens to be tested are mounted fairly level, as they should be. A piece of tar or similar material is all that is required to hold the ball in place.

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[2] For description of such measurements, see article by the writer, "Cracking of Drawn Brass," Engineering Record, April 11, 1914.

*From a paper presented at the Chicago, 1914, convention of the American Foundrymen's Association.

The test is best made by first bringing the ball just in contact with the face of the specimen. The weight on the machine is then run out to a hundred pounds or so less than the load finally desired. Pressure is next applied until the beam floats, using one of the higher loading speeds. The weight is quickly advanced and set accurately at the full load to be applied. The slow speed of the machine is then used to float the beam and keep it floating during the time required for the test.

It probably is sufficiently accurate to figure the time which the piece is subjected to pressure as beginning when the beam first rises, as the greater part of the load is then operative. After 30 seconds, or 15 seconds if the 3,000 kilogram load is being used, the pressure is released and the diameter of the indentation measured in millimeters.

It has been found that after a little practice with a fairly sensitive testing machine results can be obtained which check very well with determinations made on Swedish apparatus.

In making the Brinell test it is exceedingly important that what may be recognized as a standard set of conditions be followed. Most of the data so far published has referred to ferrous material. Much of that which has been obtained on non-ferrous alloys would often have been of more general value and application if the conditions suggested by Brinell had been followed in making the tests.

It has been recommended that a standard ball of 10 millimeter diameter be used with loads of 3,000 kilograms for ferrous materials and 500 kilograms for non-ferrous alloys. It also is advisable that iron and steel samples be submitted to the pressure for 15 seconds and alloys for about 30 seconds. The factor which has the greatest influence on the numeral obtained is the pressure applied. It has been found that elastic deformation of the sphere used is produced by the load. It is relatively greatest at the lowest pressures. Under such loads the indentation is small and the resistance offered is all in the direct line of the pressure applied. There is practically no lateral component tending to make the sphere retain its shape as when heavier loads are applied and the indentation is likely to be greater.

If the depth rather than the diameter of the indentation produced were measured, the size of the load would not be of as much consequence. It is quite likely that a linear relation exists between depth of indentation and load. It is, however, more difficult to measure the depth than the diameter of the indentation, and the latter is now almost exclusively the measurement made in commercial work.

Under all conditions the radius of curvature of the indentation is greater than the radius of the sphere. The amount varies, however, depending upon the alloy.

Table I gives the results of tests made with two different loads, each pair of determinations being made on the same sample. The hardness number was determined by reading the diameter of the impressions.

The figures in Table I illustrate the necessity of either following adopted standard methods of testing or stating the conditions under which the test was made and especially the load applied.

The diameter of the ball used does not seem to affect the test greatly, nor does a variation in the length of time the load is applied. It would seem preferable, however, especially in the absence of more detailed information concerning their effect on the test as applied to non-ferrous alloys, to follow standard methods.

TABLE I.—HARDNESS NUMERALS OBTAINED WITH DIFFERENT PRESSURES.

		Hardness under	
Alloy.	How cast.	500 kg. load.	3,000 kg. load.
Phosphor Bronze, 10 Sn	Chill	86	107
Phosphor Bronze, 20 Sn	Sand	158	196
Phosphor Bronze, 10 Sn, 10 Pb	Sand	50	69
Phosphor Bronze, 10 Sn, 10 Pb	Chill	80	103
Gun Bronze, 10 Sn, 2 Zn	Sand	70	82
Gun Bronze, 10 Sn, 2 Zn	Chill	86	107
Manganese Bronze	Sand	109	137
Manganese Bronze	Chill	119	143

Judging from the similarity of the compression and Brinell tests, it would appear that the length of time the load is applied would have some little influence on soft materials such as white metals and babbitts, which are inclined to flow under compression. It almost surely would if the load were applied for five minutes as directed in one recently published handbook, which gives directions for making the Brinell test.

Besides the variables due to the manner of testing, there are also those introduced by the sample. The effect of casting conditions upon the tensile strengths of alloys is becoming quite well known. The hardness is effected by many of the same factors.

One of the most noticeable influences is the diminution of grain size due to chilling or to *skin effect*, with a resulting increase in hardness. A large casting of red brass showed a hardness of 43 to 48 when tested inside of heavy sections. The skin on a section ¼-inch thick, of the same casting, had a hardness of 70 to 80.

As in the tensile test, chilling seems to have the most influence on the hardness in the phosphor bronzes. These same alloys are decidedly influenced by the temperature of pouring and the resulting rapidity of solidification. A phosphor bronze containing 20 per cent tin gave a Brinell hardness of 100 to 109 when poured hot. The same pattern of test piece poured cold from the same pot of metal gave 158.

Compression tests showed a permanent set of 0.070-inch per inch under a load of 100,000 pounds per square inch for the hot-poured material and 0.024-inch per inch for the cold-poured. Test bars cast in size and pulled without machining gave 23,800 pounds per square inch tensile strength for the former and 35,000 pounds per square inch for the latter. The Brinell test offers an excellent means of judging the quality of such material without going to the trouble of making compressive or tensile tests.

It is evident that the hardness of a certain alloy cannot always be expressed by one definite Brinell numeral. The best that can be said is that it usually has a hardness between certain limits depending much on the particular sample selected for test. It would be well if some standard form of test specimen could be agreed upon. The end of the cast-to-shape test bar has been found convenient by the author for comparative work.

Some idea of the hardness of a few common brass foundry alloys may be obtained from Table II. The determinations were made with a 10 millimeter ball and a pressure of 500 kilograms applied for 30 seconds. The sand cast data were obtained by using the ends of cast-to-shape test bars, and the chill cast data are from sections of small ingots cast in an iron mold.

The relation between Brinell and scleroscope hardness determinations would often prove useful if it could be fairly accurately determined. It is at times stated that to change from the Brinell number to the scleroscope reading, the former should be divided by six, and the scleroscope number multiplied by six gives approximately the Brinell numeral.

Such directions may hold for ferrous material where loads of 3,000 kilograms have been used for the Brinell tests and the universal hammer was used with the scleroscope. They do not hold, however, for non-ferrous alloys tested under 500 kilogram loads and with the magnifier hammer in the scleroscope. Further, it does not seem likely that any one factor will be found to apply for all classes of non-ferrous alloys.

The hardness test is capable of considerably wider commercial application than it has so far received. Much useful information can be quickly gained by its aid, but in order to avoid confusion and possibly self-deception, it is necessary to be familiar with the more important conditions which influence the results.

TABLE II—UNUSUAL HARDNESS OF SOME COMMON ALLOYS.

	Hardness under 500 kg. cast in	
Alloy.	sand.	chill.
Phosphor bronze, Cu 90, Sn 10	67-70	93-100
Phosphor bronze, Cu 80, Sn 20	143-158	......
Phosphor bronze, Cu 80, Sn 10, Pb 10	65-70	80-89
Gun bronze, Cu 88, Sn 10, Zn 2	65-74	86-93
Composition, Cu 85, Sn 5, Pb 5, Zn 5	48-59	63-67
Yellow brass, Cu 69, Sn 1, Zn 30	54-59	59-65
White brass, Sn 66.5, Zn 29, Cu 4.5	19-20	22-23
S. A. E. Babbitt, Sn 84, Sb 9, Cu 7	......	26.5-30.5
Manganese bronze	109-119	124-130

OPENING SOUTH CHINA COAL FIELDS.

The U. S. Consul General George E. Anderson, Hongkong, reports that there is a very fair prospect for the development of some of the coal fields of south China, especially within Hongkong's trade territory, on a modern basis. At several localities along the West and North Rivers near Canton coal fields have been worked in native fashion for some time and the output has come to amount to a considerable volume.

An American mining expert has had occasion to look into one of these fields in the past few weeks, with a view to development along modern lines, and gives some facts of interest. The property examined is situated on the North River, about 160 miles from Canton, the actual mine being located about a mile from the river bank on the right bank. The survey for the Canton-Hankow railway lines crosses the property. The property occupies broken ground, embracing two lines of hills of considerable height. The native workings are located from 800 to 1,000 feet up the side of one of these ranges and the seam has been followed down for about 400 feet. The seam ranges about 9 feet in thickness.

The native method of working is extremely wasteful and also extremely dangerous, even where the seam is so plainly exposed as it is in the case of the one worked. On this property there are three seams, one about 9 feet in thickness, the second about 2 feet in thickness, and the third about 10 feet in thickness.

The region is essentially coal country; the predominating rock is limestone intermixed with layers of sandstone and slates. Millions of tons of coal are actually in sight. The Government analyst in Hongkong reports on the analysis of a sample of this coal that 100 parts contain 0.80 per cent of moisture, 17.60 per cent of ash, 20.70 per cent of volatile combustible matter, and 60.90 per cent of fixed carbon. The percentage of sulphur is placed at 1.2 per cent, and the calorific value is 12,830 British thermal units. The ash is grayish white in color. The coke is hard, and burns with a fairly long flame.

The matter of transportation has been one of the chief factors in opening such mines. The North River, where these coal seams are found, is too shallow for successful water transportation, and there is no economical means of transport at this time. It is anticipated, however, that the Canton-Hankow Railway line will be completed to this district in about two years at the present rate of progress—that is, it can be completed to that point in that time out of the earnings of the portions of the road already completed and in operation. The completion of this line will not only immediately open up this coal field, but it will also make other fields available for the Hongkong coal market and for export.

The immediate need of these fields at present is modern machinery and capital for development.

THE DETERMINATION OF SMALL QUANTITIES OF HYDROCYANIC ACID.*

By **ARNO VIEHOEVER** and **CARL O. JOHNS.**

In our work on cyanogenetic plants we found it necessary to estimate small quantities of hydrocyanic acid. The various titration methods as well as the silver gravimetric methods had to be excluded because we were working with plant distillates which usually contain reducing compounds. Furthermore, the quantities to be determined were often too small to permit the use of the above methods. We frequently had to deal with less than 0.5 mg. of hydrocyanic acid. Chapman[1] has shown that the picric acid colorimetric method of Waller[2] is not applicable to plant distillates which usually contain reducing substances other than hydrocyanic acid. This left two colrimetric methods to be examined, namely, the thiocyanate method and the Prussian blue method.

In the thiocyanate method of Francis and Connell[3] the hydrocyanic acid is distilled into a solution of potassium hydroxide, yellow ammonium sulphide is added, and the solution is evaporated to dryness. The residue is dissolved in water, acidified with hydrochloric acid and the mixture is filtered to remove sulphur, after which the filtrate is further acidified and boiled to cause precipitation of the free sulphur. The process of boiling and filtering is repeated until all of the sulphur has been removed from the filtrate. Ferric chloride is then added to the filtrate and the color of ferric thiocyanate is obtained. After an examination of this method we found that it was not accurate enough for our work. Our two chief objections to this method are as follows:

In boiling an acid solution of a thiocyanate, some free thiocyanic acid is lost because it is volatile, the boiling point of the acid being 85°. This loss was shown by taking two equal quantities of potassium thiocyanate, diluting both portions with water, acidifying with hydrochloric acid, and boiling one of them for ten minutes in an Erlenmeyer flask. The boiled solution was then cooled. Both the boiled and unboiled portions were tested by adding equal quantities of ferric chloride. The portion that had been boiled gave less color than the one not boiled. This test was repeated and we found that in every case boiling resulted in a loss of thiocyanic acid.

The second important objection to the thiocyanate method is based on the nature of the reaction between a thiocyanate and ferric chloride, $FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$. The equilibrium of this reaction is so easily disturbed by the addition of ferric chloride, intensifying the color, or the addition of other salts, diminishing this color, that it is difficult to adjust conditions so as to obtain constant results. Changes of temperature also have a marked influence on the density of the color.

In recent years several papers have been published on the formation of Prussian blue from cyanides and the colorimetric estimation of the cyanide by comparison with a standard suspension of Prussian blue. The most careful attempts to arrive at a quantitative method seem to have been made by Berl and Delpy and by Lander and Walden.

Berl and Delpy[4] make the solution to be tested alkaline with potassium hydroxide, add a solution of ferrous sulphate, allow the mixture to stand at room temperature for at least ten minutes, shaking frequently, and finally boil for two to fifteen minutes. The resulting mixture is cooled and then acidified with hydrochloric acid. In the case of very dilute solutions of hydrocyanic acid, Berl and Delpy shake out the acidified solution with ether eight to ten times, and shake out th ether with a small quantity of potassium hydroxide solution, thus obtaining the hydrocyanic acid in a more concentrated form.

The method of Berl and Delpy has been improved by Lander and Walden.[5] These workers concentrate dilute alkaline solutions of hydrocyanic avid by boiling, the final concentrating being carried out in a test-tube almost to dryness. The small quantity of liquid left is then cooled and ferrous sulphate solution added. The mixture is allowed to stand ten minutes, with frequent shaking, then acidified with hydrochloric acid and warmed gently.

Vorländer[6] investigated the formation of Prussian blue from cyanides. He adds a solution of ferrous sulphate to the alkaline solution of the cyanide and boils for one to two minutes. He then fitlers and acidifies the filtrate with hydrochloric acid, after which he adds a cold, freshly-prepared, saturated solution of ferrous sulphate. He allows the mixture to stand until the maximum color is obtained.

Knight[7] adds to the alkaline distillate containing hydrocyanic acid, solid ferrous sulphate, then a solution of ferric chloride, and boils for one minute. Hydrochloric acid in excess is then added to the hot solution. The precipitate of Prussian blue is filtered, washed with alcohol, and dissolved in a sufficient quantity of sodium hydroxide solution. This solution is acidified with acetic and hydrochloric acids, ferric chloride is then added, and any brown color is removed by adding more hydrochloric acid. The mixture is concentrated to about one-half the original volume and the precipitate of Prussian blue, after filtration, is determined by weighing.

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*From the Journal of the American Chemical Society.

[1] The Analyst, 35, 471 (1910); 36, 269 (1911).

[2] Proc. Royal Soc. (B), 82, 574, 1910; The Analyst, 35, 406 (1910).

[3] Journal of the American Chemical Society, 35, 1624 (1913).

[4] Ber., 43, 1430 (1910).

In a method involving the quantitative estimation of a substance by means of colorimetry, it is obvious that a given quantity of the substance should always produce a given density of color in a given volume of solution. It is also necessary that the shade of color should always be the same. For instance, a blue solution cannot be compared accurately with a blue-green solution. Our aim in this work has been to obtain a constant shade as well as density of color. We have studied the following conditions which influence the formation of Prussian blue and the shade of the suspension.

INFLUENCE OF CONCENTRATION ON THE FORMATION OF PRUSSIAN BLUE.

Berl and Delpy found that they obtained less Prussian blue from given quantities of hydrocyanic acid in a dilute than in a concentrated solution. These authors, therefore, concentrated dilute solutions of hydrocyanic acid by shaking out with ether as previously mentioned. They state that in this manner nearly all of the hydrocyanic acid can be obtained. In our attempts to concentrate the hydrocyanic acid by means of ether, we found that we could not obtain nearly quantitative results. These low results are due partly to the loss of hydrocyanic acid which will occur by evaporation of the ether. This evaporation cannot be prevented at room temperature, since the acid solution has to be shaken out eight to ten times with ether. Moreover, the volume of alkali needed to extract the hydrocyanic acid from the ether will be so great that the maximum quantity of Prussian blue can scarcely be expected, as shown below.

Lander and Walden, finding also less precipitate of Prussian blue in dilute than in concentrated solutions of hydrocyanic acid, boiled the alkaline solution down almost to dryness. They state that this could be done without the loss of hydrocyanic acid.

The influence of concentration is indeed a very important factor. We made a series of experiments, using 1 mg. of potassium cyanide in each case and concentrations ranging from less than 1 cc. to 10 cc. In a dilution of 10 cc. less than one-half as much Prussian blue was obtained as when the volume was only 1 cc. We found that the maximum color was obtained only when the volume of solution to be tested was not greater than 1.5 cc., while in greater volumes the density of the color decreased with the increasing volume. Where the quantity of potassium cyanide was more than 1 mg. the volume of the solution to be tested could be somewhat increased without loss.

Hence, working with the methods of Berl and Delpy or Knight, where larger volumes than those mentioned above are used, the maximum quantity of Prussian blue would not be obtained.

To test the method of concentrating used by Lander and Walden we evaporated 25 cc. of an alkaline solution of a cyanide to 1 cc. in a distilling flask and lost almost one-third of the cyanide. When the final evaporation was performed in a test-tube the loss was less, but still considerable. Hence it appears that the method of Lander and Walden also cannot give the maximum quantity of Prussian blue, since these authors evaporate over a free flame. It may be mentioned in this connection that evaporation in an open dish on a steam bath resulted in still greater losses than those mentioned above.

After numerous failures we found that alkaline solutions of hydrocyanic acid can be concentrated without appreciable loss by distilling under diminished pressure, as described below.

INFLUENCE OF SALTS ON THE FORMATION AND PRECIPITATION OF PRUSSIAN BLUE.

Vorländer states that the presence of salts delays or prevents the formation of Prussian blue. We tried the addition of salts, because in our early experiments we often obtained what seemed to be a colloidal form of Prussian blue. Since salts are known to precipitate colloids we tried the effect of adding sodium chloride and found that a clearer blue color was obtained than without the addition of this salt. We also tried the effect of several other halogen salts. Finally, we found that the presence of potassium fluoride had a remarkable effect on the formation and color of the Prussian blue. On acidifying in the final stage of the test the color appears at once and is very brilliant. The absence of a green shade makes it particularly suitable for comparison with a standard. If the acid is added very gradually the iron hydroxides dissolve and a colorless liquid with a white precipitate is obtained. On the addition of more acid the blue color appears. This is explained by the fact that ferric salts produce a complex salt with potassium fluoride,[8] K_3FeF_6. When an excess of acid is added this complex salt is decomposed and the ferric ions needed for the formation of Prussian blue are furnished. Contrary to the statement of Vorländer, our experiments show that certain salts, such as sodium chloride and particularly potassium fluoride, hasten the formation of Prussian blue.

INFLUENCE OF ACIDS ON THE FORMATION OF PRUSSIAN BLUE AND ON THE COLOR OF THE SUSPENSION.

Previous workers all seem to have used hydrochloric acid in the final stage of the test for a cyanide to precipitate the Prussian blue. We found that an excess of this acid tends to make the color of the

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[5] The Analyst, 36, 26. (1911).

[6] Ber., 46, 181 (1913).

[7] J. Ind. Eng. Chem., 6, 909 (1914).

[8] Greef, Ber., 46 2511 (1913).

suspension green, owing to the formation of ferric chloride. The mixture of the yellow ferric chloride solution with the Prussian blue produces the green shade. To avoid the formation of the green shade we tried the effect of acids other than hydrochloric acid. We obtained good results with sulphuric and nitric acids in different concentrations. Hence these acids are recommended instead of hydrochloric acid.

Vorländer and Knight both filter off the iron hydroxides from the alkaline solution of sodium ferrocyanide and then acidify *before* adding the iron salt. This procedure may lead to a loss of hydrocyanic acid, since ferrocyanic acid oxidizes rapidly according to the following equation:

$$7H_4Fe(CN)_6 + O_2 = 24HCN + Fe_4[Fe(CN)_6]_3 + 2H_2O.$$

INFLUENCE OF FERRIC IRON ON THE FORMATION OF PRUSSIAN BLUE AND ON THE COLOR OF THE SUSPENSION.

It is to be noticed that Berl and Delpy, Lander and Walden, as well as Vorländer, used only ferrous sulphate for the formation of small quantities of Prussian blue. In the ordinary laboratory test for a cyanide, ferric chloride is also added, which changes the color to a greenish shade and makes accurate colorimetric determinations impossible. The addition of a ferric salt is not necessary, since enough of the ferrous salt is oxidized during the operation to furnish the ferric ions needed. According to our experience it is very important that there should not be a large excess of ferric salts present. Therefore, to prevent the oxidation of too much of the ferrous hydroxide to ferric, we remove most of the air from the solutions of the cyanide by means of a water vacuum pump.

In this connection we may quote Vorländer's statement.[9]

"Die Meinung ist verbreitet, dass zum Zustandekommen des Berlinerblaus aus Ferrocyankalium die Gegenwart von Ferro- und Ferrisalz nützlich sei. Ich habe hierfür nicht das geringste Zeichen finden können."

Here one might obtain the misleading impression that Prussian blue is formed in the utter absence of a ferric salt. Vorländer probably means to say that the addition of ferric salt is unnecessary, as enough of the ferrous salt is oxidized by the action of atmospheric oxygen to furnish the ferric ions needed.

INFLUENCE OF HEAT ON THE FORMATION OF PRUSSIAN BLUE.

It is interesting to note that other workers apply heat in the test for a cyanide. Sometimes the alkaline mixture is heated, and sometimes heat is applied after adding the acid. Others recommended that the mixture be heated, both before and after the addition of acid. In testing by our method heat is not necessary if potassium fluoride is used. In using sodium chloride instead of potassium fluoride, or in the absence of these salts, gentle heat hastens the formation of Prussian blue.

DESCRIPTION OF THE METHOD.

As a result of our various experiments, we recommend the following procedure: Before concentrating the hydrocyanic acid solution, as in the case of a distillate, the portion to be tested should contain a slight excess of free sodium hydroxide. We used 0.02 to 0.1 g. This solution is then concentrated in a round bottom flask of 200 cc. capacity by using a vacuum pump and condenser. The heat is supplied by immersing the flask in a water-bath kept below 70°. To avoid any loss by spattering, the flask is fitted to the condenser by means of an adapter such as is used in the Kjeldahl method for the determination of nitrogen. We concentrate until less than 1 cc. of liquid remains in the flask. Two-tenths to one-half cubic centimeter of 3 per cent freshly prepared ferrous sulphate solution and about 0.05 g. of potassium fluoride are then added. The flask is exhausted at once by means of a water vacuum pump. The contents are mixed by rotating the flask. After five to ten minutes the flask is detached from the pump and the mixture acidified with 30 per cent nitric acid. The blue color appears at once. Where only traces of hydrocyanic acid are present it is sometimes necessary to warm to about 50° in a water-bath before the color appears. The suspension is then diluted to a volume that would give a color density convenient to compare with a suspension of Prussian blue made from a known weight of potassium cyanide. As a standard we used a suspension of Prussian blue made from 1 mg. of potassium cyanide. Such a suspension diluted to 25 cc. gave a color of convenient density. For comparison we used a Duboscq colorimeter.

If the cyanide solution to be tested was sufficiently concentrated so that further evaporation was unnecessary, the test could be made in a test-tube. We kept the air out by means of a stopper and rotated the tube only enough to mix the reagents, allowing the mixture to stand five to ten minutes before acidifying. Much shaking must be avoided to prevent excessive oxidation of the ferrous hydroxide.

We ascertained the accuracy of our method by diluting 1 cc. of a standard solution of potassium cyanide to 25 cc. and evaporating under the diminished pressure to 1 cc. When the residue was tested as described above we obtained the same quantity of Prussian blue as that formed by applying the test to 1 cc. of the undiluted standard solution.

The quantities of reagents mentioned are suitable for 1 to 2 mg. of potassium cyanide. If less than 1 mg. of potassium cyanide is present, the quantities of the reagents should be reduced accordingly. A large excess of reagents must be avoided in order to obtain the maximum density of color. When the analysis is carried out as described the maximum error should not exceed more than 1 part in 20. Thus in a plant giving 20 mg. of potassium cyanide per 100 g. of plant the results might vary by 0.001 per cent if 100 g. of material are used for analysis.

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[9] Ber., 46, 188 (1913).

APPLICATION AS A QUALITATIVE TEST.

This method also proved to be a very delicate qualitative test for the presence of a cyanide. Owing to the possibility of obtaining a pure blue color we were able to detect with certainty 0.00002 g. of potassium cyanide, which represents less than 0.00001 g. of hydrocyanic acid.

APPLICATION TO MICROCHEMICAL ANALYSIS.

The test for hydrocyanic acid was applied microchemically to sections of cherry bark and bitter almond with marked success. Sections or small parts of the material were treated with the reagents in a test-tube according to our method.[10]

CONCLUSIONS.

1. Dilute alkaline solutions of a cyanide can be concentrated under diminished pressure without appreciable loss of cyanide.
2. The maximum quantity of Prussian blue can be obtained from a cyanide only when the volume of the solution to be tested is sufficiently small, as has been indicated by Berl and Delpy and by Lander and Walden.
3. In the test for a cyanide it is better to acidify with nitric or sulphuric acid than with hydrochloric, since an excess of the latter tends to produce a green color.
4. Any considerable excess of ferric salts should be avoided in testing for a cyanide.
5. Application of heat is not necessary in testing for a cyanide by the method described.
6. The presence of certain salts, particularly potassium chloride, in the liquid to be tested, has proved to be of great advantage.
7. The method furnishes a very delicate qualitative test for the presence of a cyanide.
8. The method is suitable for the estimation of very small quantities of a cyanide in distillates.
9. The test as described herein can be applied microchemically to sections of cyanogenetic plants.

The quantity of domestic fluorspar marketed in the United States during the calendar year 1914, was 95,116 short tons, valued at $6 per ton. Imports of fluorspar during the fiscal year 1914 (ended June 30) were 13,663 long tons, having an average invoice value of $3.96 per ton. Imports were much higher in previous years—23,734 tons in 1913, 22,734 tons in 1912, and 44,066 tons in 1911. The customs duty on fluorspar was reduced on October 3, 1913, from $3 a ton to $1.50 a ton. About 83.3 per cent of the domestic production marketed is gravel spar, which is used chiefly as flux in basic open-hearth steel furnaces. The market for lump fluorspar for the manufacture of hydrofluoric acid is reported to be improving. The main use of this acid is in etching glass.

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[10]Further work is in progress on the application of this method to micro-chemical analysis.

SOME NEW TESTS FOR TANNING MATERIALS.*

By **HUGH GARNER BENNETT, M. Sc., F. C. S.**

The Cobalt Test.—Whilst examining the properties of the different tannates of cobalt, the writer observed that these compounds yielded typical colors when allowed to react with hydrogen peroxide. After some experimenting the best conditions for observing these were discovered. The reagents required are:

(1) A very dilute infusion of the tanning material under examination, containing roughly about 0.1 per cent of tannin.

(2) Hydrogen peroxide of about "16 vols." strength approximately.

(3) A solution containing 1 per cent cobalt nitrate and 10 per cent ammonium carbonate. This last reagent is best made by dissolving 25 grams ammonium carbonate in a 250 cc. flask in about 150 cc. of distilled water, and then adding slowly 2.5 grams cobalt nitrate previously dissolved in a little distilled water.

The actual test is carried out as follows: 6 or 7 cc. tanning infusion (which need not be filtered) is poured in a test tube with an equal volume of peroxide, and 3 or 4 drops of cobalt solution are added cautiously drop by drop. The writer has carried out this test with nine of the most commonly employed tanning materials, and has found them to behave towards this reagent in one of three ways.

Class 1 embracing valonia, chestnut extract and oakwood extract, develops a purple coloration. If a brown is obtained the tannin infusion is too strong.

Class 2, which includes sumac (Sicilian), myrobalans and algarobilla, show an orange color. Gallotannic acid and gallic acids also give this orange color which may be regarded as another test for gallic acid. It sometimes happens (especially with myrobalans) that the first drop of cobalt solution shows a very transient purple tinge, but subsequent drops of the reagent show the color characteristic of the class.

Class 3. In these cases a bright red color immediately develops quite distinct from the preceding classes. This class embraces quebracho, mimosa bark and gambier.

Tanning materials can be divided into two classes named the "catechol tannins" and the "pyrogallol tannins," on account of the fact that on dry distillation they yield catechol and pyrogallol respectively. This division is also in harmony with many other tests, such as the bromine water test. It will be noticed by those familiar with this scientific classification, that the materials in Class 3 above all are known as catechol tans, whilst those in Classes 1 and 2 are all belonging to the pyrogallol class. It is clear, therefore, that this cobalt test provides a means for subdividing the pyrogallol division of tanning materials.

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*From the Shoe and Leather Reporter.

Some years ago the writer published in the *Shoe and Leather Reporter* a test he had devised for the same purpose, viz., the chromate test. It may be as well to describe this briefly. A tanning infusion (0.4 per cent tannin) is diluted with an equal volume of sodium bisulphite and 1 or 2 drops of a 10 per cent potassium chromate solution are added. In this case also characteristic results are obtained and it is interesting to note that the sub-division there proposed of the pyrogallol tannins, corresponds exactly with the sub-division effected by the cobalt test being described. Class 1 materials give a deep purple with the chromate test and Class 2 materials a transient blood red, which is also given by gallic acid. The two tests may therefore be regarded as confirmatory of one another and of this sub-division. Previously published tests of various other workers are also in harmony with this arrangement and it will not be out of place to mention one or two of these as they are very simple to execute. It may be understood that all may be carried out with tanning material infusions containing about 0.4 per cent tannin.

1. A few drops of this infusion are placed in contact with a crystal of sodium sulphite on a white tile or in a porcelain basin. Class 1 develop a bright purplish pink, whilst Class 2 do not give this reaction.

2. A small quantity of tannin infusion is placed in a porcelain basin and an excess of lime water added. A yellow precipitate is in each case obtained first, which quickly changes into a red purple for Class 1 materials and into a green for Class 2 materials.

3. To a small quantity of the infusion a little of a 1 per cent copper sulphate solution is added, followed by excess of ammonia. In each case a dark precipitate is obtained, but the materials of Class 1 show it with a distinct reddish tinge.

4. To 5 cc. tannin infusion add 10 cc. 10 per cent acetic acid and 5 cc. 10 per cent lead acetate solution. After mixing and filtering, add a little of a 1 per cent iron alum solution. Class 1 show no color, having been completely precipitated, whilst Class 2 all show a blue-black color.

Taking the above facts into consideration and also the results of the tests to be described later, it would seem that this grouping of the pyrogallol materials is in very good agreement. In a recently published work of Prof. Proctor, however, the formaldehyde test is chosen for distinguishing the groups. This seems very unfortunate, as this happens to be the only test which is in disagreement with all the rest mentioned above and below. The difference is that the formalin test places myrobalans in Class 1. This, however, is not only in disagreement with the other tests but also with the practical experience of tanners, who would mostly consider myrobalans as akin to algarobilla and sumac.

It is difficult to say to what the colors of the cobalt test are really due, but there are one or two points which should be noted. There is in the first place some little resemblance to the chromate test. The colors produced are somewhat alike, both for Classes 1 and 2. They both involve the use of strong oxidizing agents (peroxide and chromate) and they both involve the use of metals which usually give colored salts and compounds. In the cobalt test there is little doubt that the active reagent is ammonium cobaltate $[(NH_4)_2CoO_4]$ known to be formed by the oxidation of cobalt salts by peroxide in alkaline solution. Indeed, this green compound may be prepared first and the tanning infusion added to it. This cobaltate is then strictly analogous with the chromates. That this is the case is also shown by the fact that solutions of nickel salts (which do not form nickelates) will not give this test. It is the writer's intention to examine later the manganates and ferrates to see if they will supply analogous results. There are, however, some points of essential difference between the two tests, one being that the chromate test is in acid solution and sulphurous acid is essential to its success, whereas sulphurous acid bleaches at once the colors of the cobaltate test, which is carried out in alkaline solution. Another difference is that the typical catechols tannins (Class 3) give no reaction at all with the chromate test. Mimosa bark, however, is an exception amongst the catechols.

The Iodine Test.—Some time ago a test was published [O. Schewket, *Biochem. Zeits.*, 1913, 52, 271-274] for gallotannic and gallic acids, which was said to distinguish them from the tannins of "kino" "catechu" and "cinchona." The test consists in adding a very little weak tannin infusion to a large flask and diluting largely with hard water (400-500 cc.), and then adding about 2 cc. of a 1 per cent solution of iodine in potassium iodide. Schewket reports a red-violet color as indicating gallic or gallo-tannic acid.

The writer has been applying this test to the commercial tanning materials with striking results, and has found that many of the different tannery materials yield characteristic colors, whilst some yield no color at all. Moreover the color obtained with gallic and gallotannic acids appear to the writer more red than violet. The function of the hard water is to provide a mild alkali. If hard water is not available very weak solutions of sodium carbonate, phosphate, borate, acetate, etc., may be employed. The writer uses tap water which contains about 23 parts chalk per 100,000. This is mentioned as the color shade might conceivably be influenced by the nature and concentration of this alkali. It is surprising how dilute the tan liquor may be made and yet answer this test; indeed if any trouble is experienced with it, it is probably because the solution is not dilute enough, for it is necessary to have the iodine in excess.

The tanning materials when arranged according to this test fall into the same groups as with the chromate test and further confirm that arrangement.

1. Valonia, chestnut extract, and oakwood extract yield a dark blue color.

2. Myrobalans, sumac, algarobilla, mimosa bark, gallotannic and gallic acids yield a purple-red color.

3. Quebracho and gambier yield no color at all. It will be noticed that although mimosa bark is undoubtedly a catechol tannin (yielding a bromine water precipitate, reds, etc.) it appears to behave in some respects like a pyrogallol tannin, *e. g.,* chromate test, iodine test, and iron test. As each of these is a test for gallic acid it would appear that mimosa bark either contains gallic acid free or a gallic acid grouping in its molecule. Proctor classes it amongst "mixed and doubtful" but my own experience with the material indicates that the tannin is one chemical individual rather than a mixture. There seems no reason why a section of the catechol tans should not contain a pyrogallol grouping also.

In the reaction also the nature of the colors is obscure, and is likely to remain so for some time, as they can only be produced in such small quantities. We may note, however, that the reagent is again an oxidizing agent, and there is some resemblance to the cobalt test in the respect that the test works in the presence of a weak alkali. In harmony with the theory the writer has experimented with other oxidizing agents and weak alkalies and has found that analogous results may sometimes be obtained, *e. g.,* (1) hard water and a little bromine water, but the color is easily bleached by excess of bromine; (2) hydrogen peroxide and potassium cyanide.

Ferricyanide Tests.—It has long been known that potassium ferricyanide in ammoniacal solution gives a color reaction with tanning. This is one of the "general" reactions of tannins. A crystal of ferricyanide dissolved in a little 10 per cent ammonia makes a convenient reagent.

If, however, the test be carried out in a similar manner to the iodine test described above, different colors are obtained which classify the tanning materials almost as before. A little tannin infusion is largely diluted with hard water, and a little ammoniacal ferricyanide is added. The colors are as follows:

1. Valonia and chestnut and oakwood extracts yield a purple color.

2. Myrobalans, algarobilla and sumac yield a dark orange. The first of these three sometimes shows a very transient trace of purple.

3. Quebracho, mimosa bark, gambier, gallotannic and gallic acids show a bright orange color.

It is probable that sections 2 and 3 of this test would be better classed together for the exact orange shade may be influenced by other factors.

Another way of employing ferricyanide is to dispense with the ammonia. If the test be carried out similarly in other respects. Class 1 yield the purple color as usual, but the other materials do not react. This supplies further evidence of the close similarity of the Class 1 materials and also of the theory that the essentials are to have a weak alkali and an oxidizing agent, in this case the ferricyanide.

It is of interest to note also that here again we have a metal involved (iron) which yields colored compounds, but the iodine and bromine tests make it doubtful how far this is essential. On the whole, the explanation of these colors is probably that the tannins are in a state of higher oxidation, what may be called "per-tannic" acids, or "pertannates" being formed; these, however, are very unstable and only formed under special conditions.

Sodium Arsenate Test.—In conclusion of this article, it may be of interest to note another test which the writer has found recently to distinguish the pyrogallol from the catechol materials. It is known that a solution of sodium arsenate gives with gallic and gallotannic acid solutions a deep blue green color when the mixture is allowed to stand in air from which it absorbs oxygen.

The writer has found that if tannin infusions are diluted until they no longer color the water very distinctly, sodium arsenate then added, and the mixture allowed to stand an hour or two, all the pyrogallol tans develop a green color.

The "Class 1" materials (see above) all show a dark green, perhaps on account of their darker color.

Myrobalans, sumac and algarobilla yield a yellow green—no doubt because of the yellow dyestuff which each of these materials contains. The catechol tannins, on the other hand, develop a bright red color. This, therefore, is yet another test for distinguishing the two principal groups of tanning materials. It is the writer's intention to examine shortly the catechol tannins in more detail, and if any interesting results are obtained, perhaps it may be possible to communicate them to the *Shoe and Leather Reporter* at a future date.

PRODUCTION OF LICORICE ROOT IN RUSSIA.

According to the Transcaucasian press, states a U. S. Daily Commerce Report, the entire production of licorice root in Russia (except that of the Ural) is concentrated in the hands of one Caucasian company, which possesses four concerns in the Caucasus, one in Central Asia, three in Turkey, one in Greece, and one in Mesopotamia. In Central Asia (Tshardshui) the roots are only pressed; the further manufacture of licorice was formerly carried on at Elizavetpol (Caucasus), but this establishment was closed in consequence of the high price of fuel. The production of licorice is considered very profitable, as the root yields 30 to 40 per cent of licorice. The process of manufacture is very simple. The cost of harvesting the root is 10 kopecks per pood ($0.14 per 100 pounds) paid to the natives, and 20 kopecks per pood ($0.29 per 100 pounds) paid to the agents. At the present time some licorice root is being exported through the port of Archangel.

THE CONSTITUTION OF CHINESE WOOD OIL VARNISHES.*

By E. E. WARE and C. L. SCHUMANN.

The modern varnish operator is well acquainted with the general characteristics of Chinese wood oil, particularly those developed during the heat treatment necessary to the manufacture of high-grade rosin varnishes. He is, however, sometimes puzzled to account for the irregularities exhibited by the different shipments of raw oil, with which he is supplied. There has always been considerable difficulty in determining whether the peculiarities of the particular oil in question are due to unavoidable irregularities of the oil or to an adulteration that has not made itself manifest during the laboratory examination of the shipment.

The past difficulty in the detection of tung oil adulteration is being overcome, due to the development of methods of examination that will detect comparatively small amounts of added material. The 1915 report of Committee D1, American Society for Testing Materials, will, no doubt, do much toward standardizing the analytical methods for this oil, and by so doing will be of considerable assistance to the varnish maker in the regulation of his product.

The most characteristic property exhibited by chinawood oil is its rapid bodying at temperatures considerably below those used for other oils. This increase in viscosity continues to the point of complete solidification, even at a temperature as low as 150° C. The length of time necessary for complete solidification depends upon the temperature and ranges from 30 hours heating at 150°, to 10 minutes at 280°. This solid material, particularly when formed at high temperatures, is a non-tacky, resilient body, practically insoluble in the ordinary solvents. It is saponified only with difficulty, and exhibts other characteristics that denote a complete change in the original glyceride. Although insoluble in most solvents, this material is completely soluble in a number of the organic acids, including rosin.

The presence of air has a decided effect upon the rate of solidification, although, as has been demonstrated at different times,[1] air is not essential to solidification, which takes place perfectly well in a sealed vessel, though a longer time is required for the formation of the completely solid product. The statement of Schapringer that the effect of oxygen is entirely catalytic, and that no oxy-compounds are formed is difficult to verify by experiment. In all cases studied by the authors there have been progressively increasing amounts of oxidized materials formed, whenever wood oil or wood oil mixtures have been heated in the air. Also, if the action of oxygen be entirely catalytic, blowing air through the heated mass would hardly show such a decided effect on the rate of solidification in comparison to the rate during unagitated open air cooking. At 165° C., oil in an open dish will solidify in from 20 to 24 hours, while at the same temperature blown oil will solidify in 4 hours.

Various attempts have been made to prevent or control this solidification at high temperatures, for it is quite generally agreed that chinawood oil should impart the same superior quality to gum varnishes that it has given to rosin-chinawood varnishes as compared to rosin-linseed varnishes. The high cooking temperature of gum varnish has discouraged any extensive use of chinawood oil in this product, as the temperature is beyond the range to which the oil may be heated without solidification, and the fossil gums do not possess the solvent power for the solid material that is shown by rosin.

Several patents have been taken out covering processes to prevent solidification. One, evidently recognizing the very decided accelerating effect of oxy-acids on the time for solidification, recommends the introduction of a strongly reducing metal.[2] Another, possibly in an attempt to make use of the solvent power of free fatty acid, superheats the oil to a temperature of partial decomposition, after which it does not solidify even when heated for a long time.[3]

Investigators are pretty well agreed that the solidification of wood oil comes as a more or less direct result of the polymerization of the glyceride of elaeomargaric acid, which is the major constituent of the raw oil. This polymerization takes place through a joining at the unsaturated linkings. This, however, is not accompanied by a complete saturation, for a study of the iodine absorption of the raw and heat-treated products shows a difference of only about one-third. The polymerization is not reversed by saponification and subsequent acidification. Inasmuch as the polymerized glyceride is insoluble in the solvents suitable for molecular weight determinations, the best evidence we have that polymerization has really been effected is that the fatty acid from the solidified product has approximately double the molecular weight of the acid from the raw oil.

Morrell[4] has studied the bodying of linseed and poppyseed oils, and has shown that there occurs a similar heat polymerization with these oils, but that there is no solidification, and that the polymerization is by no means complete.

Various explanations have been offered for the solidification of chinawood oil when subjected to this heat treatment. Some experimenters believe that the solid is a uniform product of a chemical reaction which takes place at a rate dependent upon the temperature of heating and goes to completion under the proper conditions. Others take the stand that the solidification is really the development of a colloidal gel, and is not necessarily a product of complete polymerization.

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*From Journal of Industrial and Engineering Chemistry.

[1] Jenkins, J. Soc. Chem. Ind., 16 (1897), 193.

[2] German Patent 219,715, 1910.

[3] German Patent 211,405, 1908.

[4] J. Soc. Chem. Ind., 34 (1915), 105.

[5] Farben Zeitung, 18 (1913), 1171.

[6] Dissertation. Translated. Armitage and Stevens, "Chinawood Oil."

Wolff[5] claims to be able to extract the unpolymerized oil from the dry polymerized product, and he shows in his experiments that the extracted material has not increased in molecular weight, and that the polymerized material constitutes only a minor portion of the gel.

Schapringer[6] says that the solid is a final product of a double reaction, and that the polymer is well developed in the primary reaction, but remains soluble until the second reaction starts, when there is a sudden exothermic formation of the gel.

The authors are led to believe from their experiments, that the solidification is due to the formation of a colloidal gel, and, although, in the case of heated oils, a direct result of the presence of the polymer, the gel formation does not necessarily accompany the polymerization. The methods for control of solidification are simply means for hindering the gel formation, and exert comparatively little effect upon the polymerization.

A somewhat similar colloidal gel makes its appearance when the oil is treated with a solution of sulfur chloride or iodine. The time for gel formation may be regulated by adjusting the strength of solution used. In the case of the iodine-chinawood gel, the solidification may be entirely prevented by the introduction of a comparatively small amount of alcohol. This does not interfere with the formation of the iodine addition products, but acts to keep the colloid in solution.

The decomposition products formed during superheating of the oil must act similarly toward the oil in preventing solidification during subsequent heating. It is possible, by heating chinawood oil to 350° C. for only a short time, to prevent solidification from heat, even though the oil may be subjected to heating at the ordinary solidification temperatures for long periods. This still liquid product of heat treatment exhibits most of the characteristics of regularly polymerized oil. It contains a large amount of glyceride of high molecular weight, together with some free acid and a considerable quantity of unsaponifiable matter. This unsaponifiable material must exert some influence in preventing the natural solidification of the oil, for it seems hardly possible that the small amount of free acid present should act in any different manner from the same amount of free acid added to the original oil. It takes considerably more added fatty acid to prevent gel formation than has been shown in any of the superheated products with which the authors have worked.

Undoubtedly the effect of rosin upon heated oil is also one of solution or gel prevention rather than one of suspension of reaction. It should, then, be possible to show the progress of polymerization as influenced by time, temperature, and other conditions, and entirely independent of the rosin present. There might also be other reagents that would exhibit the same ability to control. The development of a nonpolymerizing wood oil will probably be along these lines.

To keep the finished product light in color, and to avoid undue loss from decomposition and volatilization of the gum, it is common practice, in varnish manufacture, to subject the oil to a preliminary heat treatment, to bring it to a body at which the final cook may be comparatively short. In the case of chinawood oil, the polymerization during this preliminary heating must be considerable, and inasmuch as this polymerization reaction is not ordinarily considered to be reversible, the function of rosin in these mixtures must be one of gel prevention.

In the experimental work, of which this paper is a preliminary discussion, the heating was carried out on the mixtures rather than on the individual constituents. The matter of color was of little consequence, and in order to get a more uniform set of results it was thought advisable to permit the rosin to exert its influence during the whole time of heating.

The first problem in the study of the polymerization of chinawood oil in the presence of rosin was the development of a satisfactory method of separation of the various possible constituents of the final mixture.

An attempt was made to use a modification of the Twitchell separation, by forming the ethyl esters of the fatty acids, and their subsequent separation from the rosin and from each other. This method gave a more or less satisfactory separation of the oils from the rosin, but the esters of the polymerized and unpolymerized oils did not show sufficiently pronounced differences upon which to base a method for their separation.

A modification of the method suggested by the authors[7] for the separation of raw chinawood oil from adulterating oils, served the purpose quite well.

The sodium soaps of the fatty acids of both the raw and heat-treated oils are insoluble in absolute alcohol, while sodium resinate is soluble in that menstruum. If proper precautions be taken for the control of temperature and concentration, the soaps of the fatty acids precipitate in a sufficiently granular form to permit of ready filtration and washing.

The subsequently freed fatty acids may be dissolved in warm alcohol of about 80 per cent concentration, from which the comparatively insoluble elaeomargaric acid may be crystallized by cooling. These characteristic crystals of elaeomargaric acid may be filtered and weighed, or the residue acids may be weighed and the elaeomargaric acid computed by difference. The oxy-acid present may be separated from the residue by precipitation from petroleum ether. In this way it is possible to get an estimation of the total fatty acid, the unpolymerized acid, the oxy-acid, the polymerized acid and the unsaponifiable.

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[7] Journal of Industrial and Engineering Chemistry 6 (1914) 806.

An extensive study of chinawood-rosin heat-treated mixtures, the results of which are now being tabulated, demonstrates quite conclusively that rosin exerts no inhibiting effect upon the polymerization of chinawood oil, either at high or at low temperatures.

THE ANALYSIS OF CHROME YELLOWS AND GREENS.*

By A. GIVEN.

From inquiries received at this laboratory, it appears that the determination of the composition of chrome yellows and chrome greens is not well understood in many color and paint works; and the excellent publications of the Bureau of Standards on the analysis of inks help only in a degree. The method here given is the result of a great deal of work and experience with these colors, and has given excellent satisfaction.

METHOD.

Moisture and Lead Carbonate—Weigh out accurately about 1 gram of the yellow or green into a small beaker, and dry for 4 hours at 105-110° C. Calculate the loss in weight as water. Add 50 c.c. of 50 per cent acetic acid to the dry substance in the beaker, mix thoroughly, and let stand over night. Filter through a tared Gooch, wash with hot water, dry, cool and weigh. Calculate the loss from dry weight as lead carbonate.

Lead Sulphate and Chromate—Weigh out accurately about 1 g., wash into a 250 c.c. beaker, add 50 c.c. water and 50 c.c. of 25 per cent caustic soda and boil for 5 or 10 minutes. Filter through a tared Gooch, was thoroughly with hot water, cool the filtrate and make up to 250 c.c. Save the residue. To 50 c.c. of the solution add an excess of hydrochloric acid and 5 c.c. alcohol and boil until the chromate is reduced to chromic chloride. Add an excess of barium chloride, boil, let settle, filter on an ashless paper, wash, burn and weigh as barium sulphate. Calculate to per cent lead sulphate.

To 50 c.c. of the above solution add an excess of nitric acid, heat to boiling and add 25 c.c. boiling saturated solution of potassium bichromate. Boil 1 minute, let settle, filter through a tared Gooch, wash, dry and weigh. Calculate as per cent lead chromate. From this amount subtract the lead sulphate and lead carbonate, both calculated to lead chromate, and call the difference actual lead chromate present.

Residue—Fill the Gooch containing the residue from the solution for lead sulphate and chromate with hot 1:1 hydrochloric acid, let stand 10 minutes, filter and wash with hot water. Repeat twice, wash thoroughly, dry and weigh. Calculate remaining residue as per cent barytes or china clay according to base.

Pure Blue—The sum of all the previous determinations is subtracted from 100, and the difference called pure blue.

REQUIREMENTS FOR CHEMICAL SOLUTIONS OF CELLULOSE.*

In the manufacture of cellulose solution for the preparation of collodion cotton, artificial silk, leather substitutes, etc., special precautions are required to be taken. The requirements are indicated in an article by C. Piest (*Papierfabrikant,* 1914, 12, 860), of which the following abstract is given in the *Journal of the Society of Chemical Industry,* xxxiii, 17:

For guncotton the material most largely employed is a mixture of spinning waste and American "linterwaste." The threads are first torn up and the lint passed through a cleaning machine to remove all mechanical impurities. Oil, natural wax, proteins, etc., are then removed by digesting with about 1 per cent caustic soda solution under 3 atmos. pressure. The material must be tightly packed in the boilers and good circulation insured; high purity of the soda and the exclusion of air during boiling and washing are advantageous. Bleaching must be very carefully controlled to preserve the chemical integrity of the cellulose; a little acetic acid may be added. The "copper value" (Schwalbe's test) must not exceed 1.0; fat and waxy matters, extracted by absolute alcohol, 0.5 per cent; wood gum, 2 per cent.

Tissue paper, from sulphite woodpulp, may also be used for nitrating but is dearer than cotton waste and yields an inferior product.

For celluloid, great mechanical purity is required to avoid specks in the product; a low "copper value," not above 1.0, is specified. For collodion cotton, long fine fibers and freedom from metallic impurities are required.

For nitro-artificial silk, resin and oil are most objectionable impurities; as highly concentrated solutions of low viscosity are employed, the degree of bleaching, as indicated by the "copper value," may be higher. Wood celluloses give a softer but weaker silk; they should be purified by boiling under pressure with dilute sodium carbonate solution with the addition of a little caustic soda or sodium sulphide.

For leather substitutes the requirements are the same as for celluloid, but a higher degree of bleaching may be permitted. For cellulose acetate, freedom from knots is an additional requirement. For cuprammonium silk also, the cotton must be free from knots and the "copper value" must not exceed 1.0. According to one process, the cotton is bleached, then mercerized, washed, centrifuged, and dissolved without drying. For viscose only wood cellulose is employed, generally purified by steeping in 2 per cent hydrofluoric acid and then boiling out with 1 per cent caustic soda; the "copper value" should not exceed 4.0.

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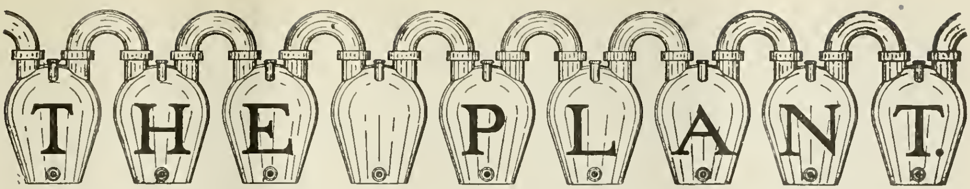
*From The Journal of Industrial and Engineering Chemistry.

*From Paper.



CHLORINE COMPOUNDS USED IN BLEACHING PULP.*

By MARTIN L. GRIFFIN AND JOHN HEDALLEN.

The experiments recorded in this paper were carried out to determine the influence of various factors on the stability of solutions of calcium hypochlorite. For this study it is important to use exact methods for determining chlorine in its various forms. We have, therefore, reviewed and tested in this connection the most approved methods for doing this, which we believe will bring some fresh knowledge to this subject.

ANALYTICAL METHODS.

Bunsen's Method.—A definite volume of bleach liquid is delivered into an excess of potassium iodide, acetic acid is added, and the liberated iodine titrated with sodium thiosulphate. This method gives the most accurate results and is a very rapid one. The only objection to it lies in the cost of potassium iodide and the somewhat unstable nature of thiosulphate solution.

Penot's method consists in titrating a known volume of the bleach with an alkali arsenite solution, using iodide and starch as indicator. This method is not very well adapted to a plant where a number of titrations have to be carried out in a short time. Since the end-point is unknown it is necessary to take out a number of samples before the titration is completed, and, finally, a check test has to be made in order to get an accurate result.

A modification of this method, by Mohr, consists in adding an excess of arsenious acid and titrating the excess with standard iodine. It has been asserted that these two methods work very well with solutions of chloride of lime, but that much trouble has been experienced in titrating the available chlorine in bleach made by passing chlorine gas into an excess of milk of lime, owing to the presence of free hydroxide, which would produce sodium carbonate when titrated with arsenious acid made alkaline with sodium bicarbonate. Further, it is asserted that the time factor will influence the titration results. We have not been able to verify any of these statements.

To examine the different methods mentioned for the determination of the available chlorine, a number of tests were made of electrolytic bleach liquor and of that made from bleaching powder with carefully standardized normal solutions. The comparative tests on the same sample were carried out at practically the same time, care being taken that conditions in each case remained the same. The same pipette was used in the same manner and the normal solutions were delivered into the sample to be tested at the same rate as when standardized.

To ascertain whether the amount of iodine used in Mohr's process had any influence upon the titration, the same sample was tested with 2, 5 and 10 cc. excess arsenious acid.

The titration results with Penot's and Mohr's methods were in every case about 0.6 per cent lower than those with the Bunsen method, and there was no indication that the electrolytic bleach liquor behaved differently from bleach liquor made from the powder.

The methods of Penot and Mohr in each case gave reasonably concordant results, and the amount of iodine introduced in Mohr's process was without influence upon the results.

We have further ascertained that the length of time used in titrating the samples is without influence, provided proper correction is made for the adhesion of the normal solution to the burette.

The method used for the analysis of a mixture of hypochlorite, chloride, and chlorate is that described in Sutton's "Volumetric Analysis" (10th ed., p. 178). The process is at once expeditious and accurate. All the determinations are performed successively upon the same solution.

AVAILABILITY OF BLEACH LIQUOR SOLUTION WITH VARYING AMOUNTS OF SLUDGE AND FRESH LIME MILK.

Base				Available chlorine (grms. per litre)				
% Sludge.	% Lime.	Total $Ca(OH)_2$ (grams. per litre).	% Excess.	Time made.	After 1 day	After 2 days.	After 3 days.	Total chlorine (grms. per litre).
100	..	33.0	10.7	20.20	2.72	2.06	1.65	28.60
75	25	32.9	11.1	22.45	2.97	2.31	1.98	28.39
50	50	32.5	12.4	24.22	4.75	2.56	2.14	27.70
25	75	32.0	13.5	26.61	26.35	26.35	26.22	27.08
100	..	52.2	81	26.45	26.40	26.35	26.22	27.72
83	17	47.2	63	27.00	26.85	26.56	26.50	27.44
62	38	42.1	47	26.95	26.95	26.95	26.85	27.55
62	38	42.1	30	30.50	30.45	30.40	30.00	31.10
35	65	37.2	23.6	28.18	28.15	28.12	27.95	28.80

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*From a paper presented before the New England Section of the Society of Chemical Industry, and later printed in the Society's Journal.

In the daily bleach plant analysis, it is hardly necessary to determine the chloride and chlorate separately, since it is only necessary to know the availability of the liquor or the relation between the available and total chlorine. The method can therefore be shortened as follows:

Pipette 5 cc. of the liquor to be tested into a pressure flask and add about 25 cc. of a solution containing 40 grammes per liter of ferrous ammonium sulphate and 40 cc. of sulphuric acid. Heat to about 100° C., cool slightly, and then add the silver, filter, wash the precipitate, and titrate the excess silver with thiocyanate as in the original process. The available chlorine is determined in a separate sample by the Bunsen method.

In the manufacture of calcium hypochlorite a certain excess of base must be present, otherwise the bleach liquor will chlorinate at once, producing a colorless or pink liquid according to the degree of chlorination, the pink color being due to manganese.

In laboratory experiments 5 per cent excess base will, as a rule, give a perfectly stable liquor with an availability of about 98 per cent even after three days' standing. In practice a larger surplus is required because, on a large scale, it is difficult to keep the concentration of the base and the volume of the feed regular, and as much as from 25 to 30 per cent excess is ordinarily used. This excess of lime separates from the liquor upon standing, and is called sludge. In the following tests, approximately 10 per cent excess base has been used, calculated on the total chlorine in the liquor. The availability obtained with lime alone as a base is taken as a standard in comparing the results.

LIME SLUDGE.

The considerable excess of lime used in the manufacture of calcium hypochlorite can be used over again to advantage under certain conditions. It differs from fresh lime in that it does not possess the same ability to form a stable hypochlorite, though the excess of calcium hydroxide be the same. This is mainly due to the impurities.

The following analysis gives the relative composition of lime and its corresponding sludge:

	Lime. %	Sludge. %
CaO	96.5	81.0
MgO	1.0	5.5
Fe_2O_3,Al_2O_3,SiO_2	2.5	13.5

To determine the effect of sludge upon the availability when used over again for the manufacture of hypochlorite several tests were carried out with varying amounts of sludge and fresh lime as a base. The free calcium hydroxide in the sludge used was determined gravimetrically. The results are given in the following table, from which it may be seen that in the first four tests respectively 100, 75, 50 and 25 per cent sludge was used in conjunction with 25, 50 and 75 per cent fresh lime.

It will be seen from the table that the bleach liquor is unstable with sludge alone and with 75 and 50 per cent sludge when the excess base is only about 10 per cent. All of these samples turned pinkish shortly after being made, and after three days standing 16.5 per cent of the total chlorine had been converted into chlorate. The fourth sample with 25 per cent sludge and 75 new lime gave a stable liquor of 96.8 per cent availability after three days' standing. These results correspond to what we have found in practice.

These tests were repeated with the same amount of new lime but with a more concentrated sludge. In this case we found, as shown in the table, that sludge alone, as well as 75 and 50 per cent sludge, will give a bleach liquor of a fairly high availability when well protected by an excess of calcium hydroxide, even in the form of sludge.

INFLUENCE OF ALUMINUM, MAGNESIUM AND IRON HYDROXIDE.

The impurities occurring in ordinary lime are aluminum, magnesium and iron oxides; silica may be left out of consideration in this connection. To determine to what extent these impurities affect the availability of hypochlorite solutions, varying amounts of each were added, as freshly precipitated hydroxide, to the lime milk and the results noted on each of three succeeding days. The impurities added in each case were 2, 5 and 10 grammes of hydroxide per liter, the

EFFECT OF TEMPERATURE AND CONCENTRATION UPON THE AVAILABILITY OF BLEACH LIQUOR SOLUTIONS

(A) Concentration

Base		Strength of liquor	Available chlorine (grms. per litre)			
$Ca(OH)_2$ used (g. p. l.)	% Excess	Total chlorine (grms. per litre)	Time made	After 1 day	After 2 days	After 3 days
172.6	9.9	150.5	147.88	146.90	146.20	145.00

(B) Temperature

Base		Temperature ° C.	Total chlorine (grms. per litre)	Available chlorine (grms. per litre)			
$Ca(OH)_2$ (g. p. l.)	% Excess			Time made	After 1 day	After 2 days	After 3 days
31.7	11.7	30	27.20	26.99	26.96	26.96	26.90
31.7	12.21	35	27.05	26.81	26.80	26.80	26.76
31.7	11.3	40	27.30	26.90	26.82	26.82	26.78
31.7	9.4	45	27.80	27.30	27.30	27.22	27.22
31.7	6.3	50	28.60	28.00	27.98	27.98	27.98
31.7	4.2	55	29.20	28.55	28.53	28.52	28.52
31.7	10.0	60	27.62	27.00	26.96	26.96	26.90
31.7	7.9	70	28.15	27.42	27.42	27.40	27.40
31.7	8.6	80	28.00	27.30	27.21	27.30	27.19
31.7	11.3	90	27.30	26.50	26.42	26.42	26.40

calcium base used being equivalent to 32.1 grammes per litre of $Ca(OH)_2$. Chlorine was led into these mixtures until the excess of calcium hydroxide remaining was approximately 10 per cent.

Considering first the influence of aluminum hydroxide, we find that as much as 2.0 grammes per liter is without influence upon the stability of the liquor in the presence of 10 per cent excess calcium hydroxide. Neither will an amount of 5 grammes per liter affect the availability, provided about 10 per cent excess base is left; however, in the case of 5 per cent excess calcium hydroxide, the availability drops rapidly, leaving only about 18 per cent of the chlorine as hypochlorite after three days' standing. The solution is stable with as little as 5 per cent excess base in the absence of impurities.

In the case of 10 grammes per liter of aluminum hydroxide the availability is noticeably affected. Thus with 13 per cent excess base, the availability was 95.4 per cent after three days, and with 8.5 per cent excess, the available chlorine was reduced to about 20 per cent after three days. These experiments go to show that the influence of aluminum hydroxide largely depends upon how well the liquor is protected by the alkaline calcium base. Further, when as much as 10 grammes per liter of this impurity is added it will depress the availability of the hypochlorite solution even in the presence of a large excess of calcium base.

The magnesium hydroxide was added as Phillips' milk of magnesia. It has no influence upon the stability of calcium hypochlorite solutions in the presence of about 10 per cent excess calcium hydroxide. On the other hand it does not replace the calcium as a base; thus in the presence of 10 grammes of magnesium hydroxide per liter with an excess of calcium of only 0.5 per cent, the availability dropped to 37.6 per cent after three days.

Ferric hydroxide, on the other hand, even in small quantities, rapidly reduces the availability of the calcium hypochlorite solution, leaving a pinkish liquor; its influence is proportional to the amount added.

Stability of hypochlorite solutions with alkaline earths, alkali metals, and magnesium hydroxide as a base.—The bleach liquor samples in these cases were made in the same way as the previous ones. The temperature of the base, the concentration of the liquor, and the excess alkalinity were the same for each test. Both the alkaline earths and the alkali metals gave practically equally stable hypochlorite solutions, with an availability above 98 per cent after three days standing.

The stability of the liquor obtained by leading chlorine into magnesium hydroxide (Phillips' milk of magnesia) is quite dependent upon the excess of free alkalinity. Thus, in the first test, where only half of the alkalinity was used up, 75.5 per cent of the total chlorine was present as hypochlorite after three days, while in the second test, where only 26.5 per cent of the total base was left as free alkali, the availability dropped rapidly to 7.9 per cent.

As a rule it can be said that in leading chlorine into magnesium hydroxide under the same conditions as in the case of calcium hydroxide, the hypochlorite at first formed will change rapidly to chloride and chlorate with about 16 per cent of the total chlorine present as chlorate.

Bleach liquor made with magnesian lime as a base.—To show further the effect of magnesium hydroxide upon the stability of calcium hypochlorite solutions, a number of tests were repeated with ordinary magnesian lime containing calcium and magnesium in the proportion of 60 to 40, besides impurities to about the same extent as in the calcium lime used in these tests.

Stability of hypochlorite solutions with magnesian lime as a base.—In the first series of tests the total alkalinity of the base used was equivalent to 34.42 grammes of calcium hydroxide per liter, with an actual amount of calcium hydroxide of 18.5 grammes per liter. The first three samples gave a stable liquor of about 98 per cent availability since they contained a large excess of calcium base. In the three last samples the total chlorine exceeded the alkalinity of the calcium present; the availability of all of these samples dropped rapidly to about 7 per cent after three days' standing.

A second set of tests was repeated with the object of determining more closely the relation between the excess calcium and the availability of the bleach liquor. When the total chlorine was equvalent to 90 per cent of the calcium present the liquor was perfectly stable, while with 4.8 per cent excess calcium base the liquor was stable for only one day, after which the availability dropped about 5 per cent a day. Moreover, when the total chlorine was just equivalent to the calcium base the availability dropped regularly about 5 per cent a day. In going beyond this limit the depression of the availability increased more rapidly.

In these two series of tests the calcium base used was only about half what it had been in the previous tests with calcium lime as a base. A third set of tests was therefore carried out with magnesian lime. The total alkalinity of the base was 61.5 grammes per liter expressed as calcium hydroxide. In the first two samples the excess calcium was 10 and 5 per cent, respectively, and the availability of the bleach liquor 98 per cent after three days. In the next sample a trifle more chlorine was led than corresponded to the alkalinity of the calcium present. This sample soon turned pinkish and the availability fell rapidly to 12.1 per cent. In the other samples the total chlorine was gradually increased until the excess alkalinity dropped to 10 per cent. The samples turned pinkish as they were made and smelled strongly of chlorine. The liquor proved very unstable. After three days the pinkish colored samples contained 15 per cent of the total chlorine in the form of chlorate.

The effects of magnesium upon hypochlorite solutions may be summarized thus:

1. The magnesium hydroxide has no effect upon the availability of calcium hypochlorite solutions provided the liquor is protected by at least 5 per cent calcium base.

2. The magnesium hydroxide sustains the stability of the hypochlorite solutions to some extent when the excess calcium is between the limits of 0 per cent and 5 per cent.

3. Even a large excess alkalinity in the form of magnesium hydroxide is incapable of maintaining the stability of calcium hypochlorite when the calcium is exhausted.

4. The absorption of chlorine after the calcium is consumed is very incomplete.

5. When leading chlorine into a mixture of calcium and magnesium hydroxides no magnesium will go in solution before all of the calcium is exhausted.

In order to make this work more complete similar experiments were carried out, using small amounts of all the elements of the iron group, including iron, chromium, manganese, nickel and cobalt. In each case the bleach liquor was very unstable, even when well protected with an ample excess of calcium hydroxide.

To determine the influence of concentration upon the formation of hypochlorite and the stability of solutions of high density, chlorine was led into a suspension of calcium hydroxide of 172.6 grammes of $Ca(OH)_2$ per liter until a concentration was reached of 105.5 grammes of total chlorine per liter, leaving 9.9 per cent excess base.

The availability of this liquor as made was 98.2 per cent, and after one, two and three days, respectively, 97.5, 97.2 and 96.3 per cent.

From these results it appears that the concentration of the liquor has very little effect upon its stability. Stable bleach liquor of lower densities is usually greenish in color, while at a high density it is yellowish. Bleach liquor of course settles more slowly with increasing concentration.

The effect of temperature was next examined by leading chlorine into calcium hydroxide at varying temperatures, starting at 30° C., and increasing the temperatures by 5° up to 60° C., then increasing the temperature by 10° up to 90° C. The table shows the temperatures of the finished liquor. The chlorine was led into the base at such a rate that the sample was finished in half an hour. The total chlorine and the excess base were in each case about the same.

From the table on the preceding page it is seen that even high temperatures have very little effect upon the availability, it being decreased only 2.20 per cent by raising the temperature from 30° to 90° C.

Under date of July 28 Consul John M. Savage reports that Sheffield prices for ferrotungsten have risen to \$1.64 per pound of tungsten contained in the alloy and tungsten powder (96 to 98 per cent pure) to \$1.82 per pound.

COMMERCIAL GLUCOSE AND ITS USES.*

By GEORGE W. ROLFE.

Most well-informed people know that in the early part of the last century Kirchoff was the first to describe a sugar made by boiling starch with dilute sulphuric acid, and that this sweet, subsequently found to be other than cane-sugar, was called "glucose" or "grape-sugar." Later it was termed "dextrose" when in the progress of science it became necessary to distinguish the individual from a whole family of "glucoses" which had been discovered.

Nowadays, most of us have heard of "glucose" as a commercial product of doubtful reputation. People look askance when glucose is mentioned. Confectioners and grocers make haste to deny that glucose ever appears in their products. Glucose is classed with harmful food adulterants, and has been called by pure food experts the "champion adutlerant" of all. It has been depicted in cartoons as a devil with hoofs and horns. Glucose has also been called "mucilage," the implication being that it is only fit for postage-stamps and not for human stomachs. This may be why many associate glucose with glue. The names sound alike and both are sticky, but the reasoning is like assuming that all gentlemen are gentiles. Glucose makes a rather poor adhesive, but one who is hard put for mucilage might so use it with indifferent success just as it is possible to use tapioca pudding, molasses or other sticky foods.

Turning to the advertising literature of the glucose manufacturers, we note that many eminent authorities laud glucose as most wholesome, that it is the principal sweet of fruits and one of the intermediate products of the digestion of starch in the human organism, is found in the blood—and similar statements, all of which, like the damning ones of some pure food experts, are "important if true."

Notwithstanding that annually between thirty and forty million bushels of Indian corn are made into glucose, comparatively few except those engaged in the numerous industries in which glucose enters ever see the product. The idea of the general public, professional as well as the laity, seems to be that glucose is mostly composed of grape-sugar, which is made according to the Kirchoff method by boiling starch and oil of vitriol and neutralizing the mixture with chalk. Many supposedly up-to-date cyclopedias make such statements.

Much of the ignorance concerning this important food product is due to the following facts: Pure commercial glucose is practically unknown in household cookery, and so is not sold in a package convenient for household use. While it is in multifarious food products found on the grocers' shelves, it is rarely seen there in its original state. This is equally true of raw sugar. Years ago, raw open-kettle sugars were familiar to all New England housewives and were used by them in cooking. Raw sugars made by modern processes are used to some extent now in England and European countries, but nowadays few of the citizens of this country, outside of the sugar producing districts, ever see raw sugars, which are sent directly to the refineries in packages weighing several hundred pounds each and in a condition not fit for domestic use. Glucose, like refined sugar, is manufactured in comparatively few factories, and these of large capacity, for the manufacture of glucose requires a large outlay of capital and consequently large output. The cheapness of the product makes its manufacture profitable only on a large scale. This is equally true of sugar.

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*From Science Conspectus, Vol. 5, No. 1.

What is commercial glucose? In general appearance it is a transparent, very viscous syrup, often practically colorless, but usually of a light straw color, sweet, but with little if any other flavor. For this reason, glucose, like sugar, has been termed a "neutral sweet"—not neutral in the chemical sense—although such products are always chemically neutral within practical limits of testing—but so called because when pure they have no characteristic flavor other than sweet and will take any added flavor unchanged.

Glucose is not made by use of oil of vitriol and chalk, nor is glucose, in the ordinarily accepted sense of dextrose, its characteristic ingredient. The trade name "glucose," while well established by custom of years, is no more suited to the present product than is "chloride of lime" to bleaching powder or "hyposulphite of soda" to the commercial salt sold under that name. It is true that the basic process by which glucose is made from starch is on the lines of Kirchoff's original experiments, but the methods are quite different. The "starch milk," a suspension of the granules in water, is pumped into large pressure boilers of gun metal, and is cooked for about ten minutes with a few tenths of a per cent of hydrochloric acid (commercial muriatic acid) under a pressure of about 50 pounds of steam. The starch is not treated long enough by this process to convert it entirely into grape-sugar (true glucose), only about 20 per cent being produced. There is, in fact, less of the glucose sugars, properly so called, in commercial glucose than occur as natural ingredients of cane-sugar molasses, and far less than in honey, which is composed almost entirely of glucose sugars, nearly half of which is dextrose (grape-sugar), this being the sugar which separates out when the honey granulates.

Commercial glucose as now made contains less than 20 per cent of true glucose sugars, the rest being a mixture of malt-sugar (maltose) and dextrins, more or less in chemical combination in the approximate proportion of nine parts of maltose to seven of dextrin. In percentages of total sugars and dextrins, there are, in round numbers: maltose, 45 per cent, dextrose, 20 per cent, dextrin, 35 per cent, the proportions varying somewhat in different lots.

These three carbohydrates, *dextrose*, which is a true glucose sugar, *maltose*, belonging to the cane-sugar family, and making up nearly half of the total, and *dextrin*, a gummy ("colloidal") substance closely related to starch paste, compose over 99 per cent of the solid matter of refined commercial glucose. This composition has been found to be the most desirable for imparting to the product the properties most suited for a syrup which can be refined readily, and at the same time contain enough colloidal material to prevent its crystallizing at any concentration. This colloidal matter also renders the syrup capable of dissolving considerable amounts of cane-sugar without crystallization. Such a product is peculiarly valuable in the preparation of syrups, candies, preserves, and jellies, quite apart from its use as a sweet. It also contains nearly the maximum amount of malt sugar that can be produced by such a process.

The rest of the dissolved substance of commercial glucose consists of 0.3 to 0.5 per cent of mineral matter, mostly composed of sodium chloride from the neutralization with soda of the hydrochloric acid used in the manufacture, sulphites which are added at various stages, phosphates and other salts from the natural mineral matters present in minute quantities in the starch or coming in part from the bone-black used in the refining process. There is also about 0.08 per cent of nitrogen, corresponding to five or six times its weight of organic substances from the gluten left in the starch. Much of this nitrogenous matter is not gluten, but simpler organic compounds resulting from the action of the acid (used to convert the starch) on the gluten. These nitrogenous matters have much to do with the quality of the glucose, and it is on this account that they are of peculiar importance, although present in minute amounts. The impurities from the gluten which are less acted upon by the acid, the "albumoses," give trouble to the candy manufacturer by causing foaming in his kettles, while this property is the joy of the brewer. Those gluten substances which are changed further by the acid, the "amino bodies," tend to make the glucose darker and also impart a flavor which, though barely perceptible, is disagreeable—bitter or fishy. Manufacturers used to correct the objectionable effects of these impurities by the addition of sulphites to the glucose, but this was but a temporary expedient and undesirable in a food product. Glucose has been much improved in recent years by practically eliminating the effect of these impurities by more efficient purification of the starch used in its manufacture.

The glucose process does not end with the acid treatment of the starch and the neutralizing, as at this stage the dilute syrup is far from pure, containing oily matters from the corn, some undecomposed gluten and other impurities, mostly in suspension. This liquor before it is concentrated to a syrup of about 80 per cent solids undergoes a refining with bone-black closely resembling that of cane-sugar, the apparatus being practically identical—filtering through bags and bone-black filters—but in the case of glucose all impurities affecting the quality of the syrup have to be removed or destroyed, as there is no purification by crystallization.

Hence glucose, like granulated sugar, is one of the purest food products in use, however pernicious the properties that may be ascribed to it.

Space does not allow a detailed description of glucose manufacture, which is of great interest, owing to the numerous by-products which are made, and also because, while glucose is the chief in output, its manufacture is only one of many starch products carried on at the same time.

The following table, taken from an advertising circular of a manufacturer, shows in a concise way how the different parts of the corn kernel are utilized:

Parts of corn kernel.	Composition.	Products.
1—Germ	Oil and oil-cake	Corn oil, corn oil-cake, corn oil meal.
2—Endosperm (body of the corn)	Starch	Dry starches, dextrins, and, by conversion, corn syrups (glucose) and sugars.
	Gluten	Gluten feed.
3—Hull	Bran	
4—Water added for steeping	Soluble substances of corn	

The oil is used principaly for soap and for making vulcanized products used for rubber substitute. The oil-cake and meal from the cake are used as cattle feed. The gluten and bran from the starch, mixed with the soluble matters extracted by the water used to soften ("steep") the grain before grinding; is made into "gluten feed," also for cattle. All these are valuable by-products for which there is a good market. The starch in a moist state, known as "mill starch," is the raw material for making the various goods which are sold under the names of "glucose" ("corn syrup"): "corn-sugar" ("grape-sugar"), the latter a hard product which is largely composed of dextrose, but never known in trade as "commercial glucose" and little used as a food product; "dextrins," true adhesives which are usually made by roasting starch and entirely different in characteristics from the dextrin ingredient of commercial glucose; besides numerous "dry starches" used by laundries, confectioners, and in many other industries, as well as for household purposes.

At present prices commercial glucose, a syrup containing about 80 per cent of the pure carbohydrates in solution, sells at about 2¼ cents per pound (26 to 28 cents per gallon), or at about 2.7 cents per pound of actual dissolved substance. Is its sole use that of an adulterant of better food materials, as some food reformers claim? Is glucose used to adulterate our ordinary grocery sugars?

It is well known in the history of the industry that some thirty years ago a Chicago concern spent some millions of dollars and much valuable time in trying to adulterate fine-grained white sugars with solid grape-sugar of high quality, made from starch, but the attempt failed miserably, simply because the stuff would not stay mixed and the grains "set" in a solid mass after a short time. In years gone by, glucose was also much used to mix with cheap, poor-grade molasses, making a brighter, more attractive product which, so improved, could be sold at the price of higher grade molasses. This form of adulteration is so easily detected that it is rarely resorted to in these days of pure food legislation. The last case which came to the writer's notice was one of a New York molasses dealer who was heavily fined for having a few per cent of commercial glucose in his molasses, although his defense was a plausible one—that the glucose was some accidentally left in the barrel, old glucose barrels being much used for tropical molasses shipments.

Glucose is now used in a legitimate manner to mix with cane-sugar syrup in the proportion of 85 per cent of glucose to 15 per cent of syrup, a little salt and sometimes vanillin being added to improve the flavor. The cane-sugar syrup is usually refinery molasses ("barrel syrup"), which imparts the principal flavor. These mixed syrups are sold openly as glucose or "corn syrups," and as their flavor is superior to the original molasses there seems to be no reason why they are not wholesome food products for legitimate trade, even though some people there are who prefer the flavor of the syrups made from the natural cane juices and are willing to pay the higher price for such. Certainly, such glucose syrups are preferable to the average grocery molasses, either from the standpoint of the epicure or the sanitarian.

Commercial glucose is used in large quantities in the manufacture of cheap jams and preserves. Apple cores and skins from fruit in its preparation for evaporation or preserving are the basis for most cheap jellies; the pectin substance and juice being extracted by the usual processes of jelly making and mixed with glucose and sugar forms a jelly material to which other fruit juices are added. The law requires such jellies to be plainly described on the label so that the consumer is informed that he is using a jelly made of apple and glucose with a fruit flavoring, and is at perfect liberty to buy the pure, glucose-free fruit product if he so prefers. What interests the public is: Are these cheap jellies unwholesome, or is there other reason why the man with the slim pocketbook should not buy them? This question is quite apart from whether they contain glucose or not, but deals with the soundness and wholesomeness of the ingredients used and the cleanliness of their preparation.

By far the largest amount of glucose is consumed in the manufacture of candy, the peculiar properties of this syrup making it especially valuable in this industry, as has been explained. The requisite for most candy is that it should not "grain" (crystallize), and glucose, owing to its colloidal nature, is the most effective and wholesome substance to prevent this. The popular impression that glucose is used in candy-making because it is a cheap substitute for sugar and that its sole function is to give sweetness is only approximately correct.

How sweet is glucose relative to cane-sugar? Determinations of the sweetness of saccharine product are very unsatisfactory, owing to personal equation and also to the influence of the other mixed ingredients and even the physical condition of the substance tested.

Granulated sugar tastes sweet. Powder it in a mortar and it will taste less sweet. Owing to this fact it is hard to convince some people that powdered sugar is not adulterated, although this practice, easily detected, is practically unknown at present. A quarter of a grain of quinine mixed into a pound of granulated sugar is said to make it taste sweeter. Common salt in small quantities will improve the sweetness of cake and other sweet foods, as all cooks know. Raw sugars, even when they contain negligible quantities of the sweeter mother-syrups, taste distinctly sweeter than granulated sugar, although their actual sugar content is less. This is due to the salts and extractive matters in the raw product, and it is why many cooks sigh for the old-fashioned, open-kettle sugar, and even prefer the refiners' imitation goods to granulated in making their apple pies.

Relative tests of the sweetness of cane-sugar and glucose (*dextrose*) have been made by dilution experiments on the pure sugars, but, so far as the writer knows, no relative tests of the sweetness of commercial glucose as now made have been published. Taking this value to be 0.5 for the solids in glucose, sugar at 5 cents is cheaper as a sweetener than glucose.

As a matter of fact, very little candy is made with glucose as the only sweet. Usually, candy contains 60 per cent or more of cane-sugar, the sweetening of the glucose being of much less importance than the other properties it imparts to the mixture.

It seems reasonable to infer that commercial glucose, rather than being a serious competitor of cane-sugar, has really increased the consumption of the latter, especially in candies. Because of the great advantages from the use of glucose in candy-making, the industry has had an impetus which has greatly increased sugar consumption.

The relative wholesomeness of candies made from glucose and those made from cane-sugar has never been decided, and may never be. The dextrins of "glucose" as now manufactured are in great part in combination with the malt-sugar and seem in every way identical with the malto-dextrins obtained by the action of malt on starch, and are digested more in the intestines than in the stomach as compared with pure sugar candies. Whether this is an advantage or not, the physiologists must decide.

Glucose is extensively used in industries not making food products. It is used in cheap soaps, for "filling" leather and tanning extracts, and, as many of its uses in such industries are apparently for adulteration, such practices have no doubt added to its reputation as the "champion adulterant." As was pointed out in an article in a previous number of this magazine,[1] on the industrial uses of sugar, the highly respectable beet-sugar of 99 per cent purity is used in Europe for precisely the same purposes, the choice between sugar and glucose as a "filler" being merely a matter of price. Cane-sugar has also been used extensively to "fill" coal-tar dyes and adulterate chocolate without having its respectability seriously impugned.

In view of the undoubted commercial importance of glucose as a food product it would seem as if its value in dietetics and food economics, as well as its relative wholesomeness, ought to be studied in the light of a proper knowledge of its special characteristics. To call glucose "mucilage," or to ascribe to it properties of a dextrose solution, is either ignorant or dishonest. So far as the use of glucose as an adulterant is concerned, it is the function of the pure food laws to protect the public from these practices, and such obviously are quite apart from the legitimate and open use of glucose, sugar, or any other cheap and wholesome food product as a satisfactory substitute for more expensive ingredients, and the propriety of such a substitute always will be its suitability for the purpose and its cost.

If legislation is appropriate for forbidding the extravagant claims of manufacturers and dealers as to the superiority of their food products, why not legislation to prevent irresponsible statements of "pure food" authorities which are condemnatory? Certainly, the one is as important for the public interest as the other.

Magnesite Deposits in British Columbia.

The U. S. Consul General, R. E. Mansfield, Vancouver, Canada, reports that magnesite, one of the most valuable of the nonmetallic minerals, has been found in large quantities along the shore of Lake Atlin, in the northeastern part of British Columbia. Seven claims have been located by Vancouver parties, and plans are being made for working the deposits. This ore is shown by analysis to be exceptionally pure, running as high as 98 per cent in magnesium carbonate. The world's supply has so far come from California, Greece, and Austria. On account of the war the latter source is cut off, and since this was the most important, there is an extraordinary demand for the mineral which British Columbia will soon be in a position to supply.

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[1] Science Conspectus, No. 2, 1913.

THE MANUFACTURE OF ALCOHOL FOR USE IN PERFUME.*

The subject of alcohol, and even limiting it to cologne spirits, covers rather a wide field, and it will be necessary to skip some of the details in its manufacture, but at the same time I would like to go somewhat into detail about the manufacture of alcohol from the bottom up, in order to bring out some of the points of most interest to the manufacturing perfumer.

Alcohol, as we all know, is produced by fermentation of various saccharine products, whereby these various sugars during the fermentation are split up into alcohol and carbonic acid. Besides that, there are formed various by-products, and it is the by-products we have to contend with in getting a pure alcohol fit for the perfumer's use.

The various raw materials we employ in the manufacture of alcohol are quite considerable in number, and the most important of them are grapes, sugar beets, cane-sugar molasses, potato starch and the various grains. In the case of grapes, these contain sugar which is directly fermentable and splits up easily under the action of the yeast. In the case of cane-sugar molasses and beet sugar, the raw product to be fermented is cane sugar, which first must be hydrolized in order to be fermentable. This hydrolization or inversion is easily carried on by the invertase contained in yeast.

When we have to do with starchy material, such as potatoes or grains, it is a more complicated process. To begin with, these products must be first converted into sugars, which are fermentable. The conversion can be carried on by various means, but in this country it is nearly always done by means of malt. Malt contains an enzyme called diastase, which has the power of converting starch into sugar, such as maltose, converting about 80 per cent of the starch into this sugar. The conversion is very rapid after the starch has been boiled to form a soluble starch. The process is carried on at a temperature of about 60 degrees Centigrade, and the conversion is completed in about twenty minutes. Then the mash is ready to be mixed with yeast and run into the fermenting tubs.

There is another interesting process for converting the starch into sugar that has been used in Belgium and France of late years, called the Amylo process, and the enzyme which causes the conversion is found in the fungus called Aspergillus oryzae. It is really a very old process that has been carried out in the East, in Japan and China, for centuries, but it has not found any practical application in other countries until within the last thirty years or so. It was tried in this country some years ago by a big plant in Peoria, but that plant abandoned this process, and only lately, I think last year, it has been tried again and proved successful.

The process is very much more rapid than the malt process, and the following fermentation is about two days more rapid than with sugar converted from starch by means of malt, and the alcohol obtained from it is very pure. The first crude alcohol, distilled from a mash made according to this process, has a peculiar odor and musty taste, but after it has been purified by rectification it is very good, both for potable spirit and pure cologne spirit. It has, I think, a great future, because this process is considerably cheaper than the malt process, both because it is cheaper than the malt, and also on account of the great saving of time in the process.

After the starch has been converted into sugar it is ready to be pitched with yeast.

In the case of cane-sugar molasses we have some difficulties to overcome before the fermentation. In the first place, molasses contains quite a large amount of nitrates which would act as a disinfectant and stop the fermentation. It also contains free alkali, and fermentation will only take place in an acid solution and, besides, it contains some of the salts of various fatty acids such as of acetic and butyric acid, which also have a tendency to arrest the fermentation.

The first step is to dilute the molasses until it contains about fifteen per cent of sugar, and then it is acidified by sulphuric acid, thereby neutralizing free alkali. By following heating the nitrates are destroyed, volatile acids are boiled out and the various bacteria which the molasses contained are destroyed and, after cooling, the molasses will be ready to be pitched with the yeast. The fermentation is generally started at about 20 degrees Centigrade, and during the first two days the temperature rises very quickly to about 30 degrees Centigrade. Then it stops rising, and during the after fermentation, which will last about three days, the temperature falls again to 24 or 25 degrees Centigrade.

After five days, as a general average for grain mashes, the mash is ready for distillation in the big continuous distillation apparatus which is used nowadays. The apparatus consists of a big column still, about forty-five feet high, which is divided into a number of smaller compartments, each of them really acting as a small still. The mash containing the alcohol flows in at the top and flowing down through the various small compartments, meets a current of steam which drives off the vapors of the alcohol, and, in going from compartment to compartment, the vapors naturally get richer in alcohol, until at the top they enter into the condensers.

By this distillation we obtain a very crude alcohol containing all the impurities, and from this point we will take up the process which is of most interest to you, namely, the manufacture of cologne spirits. All crude alcohol contains, comparatively speaking, a lot of impurities, and the impurities are what we have to consider in making pure spirits. Of late years it has been possible to check the formation of these impurities to a very great extent. For many years it was thought that the formation of the so-called higher alcohols, such as amyl, butyl and propyl alcohols was caused by side fermentations from the sugar. It has, however, been proven by Dr. Felix Ehrlich that these higher alcohols forming the so-called fuse oil are not formed from the sugar by side fermentation, but formed from amino-acids contained in the raw material from which we started. The yeast during its growth requires nitrogen and this it obtains from the amino-acids, thereby causing the formation of alcohols of a higher atomic weight than ethyl alcohol. Dr. Ehrlich also found that the addition of an inorganic salt, such as ammonium sulphate, greatly checks the formation of these higher alcohols, because the yeast assimilates more readily the nitrogen from this salt than from the more complex organic amino-acids.

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*From The American Perfumer.

Another thing of interest to the perfumers is that phenyl ethyl alcohol, of which we use a great deal, is found among the higher alcohols formed during this fermentation, and a few years ago Dr. Ehrlich took out a patent for the manufacture of this alcohol by such a fermentation process, but I do not believe it has proven any great commercial success.

If we now want to consider the purification of the crude alcohol, we must first consider the composition of these compounds that we want to eliminate. We can divide them into two classes, the compounds which are more volatile than the ethyl alcohol, and the compounds of higher boiling point. Among the first we have aldehyde. Most of you know the odor of that from commercial alcohol. Among other impurities of lower boiling point than ethyl alcohol we can mention ether, ethyl formiate acetate and methyl acetate. All of these will, during the rectification, pass over with the first distillate. The art of purifying the crude alcohol nowadays is nearly always done by a fractionate distillation, and carried out in big stills, very similar to the one in which the first distillation takes place. A column still is mounted on top of a big copper kettle, into which a charge of about 10,000 gallons is put. The distillation begins and the first part of the distillate is put aside for later rectification. This part contains the aldehyde and the various volatile constituents of a lower boiling point than the ethyl alcohol.

If we now continue the rectification we get the product which is called cologne spirits or neutral potable alcohol, which, after being aged for one or two years, forms the cologne spirits which the perfumer uses.

The last part of the distillate contains the alcohols of higher atomic weight, such as amyl alcohol, isopropyl alcohol, normal propyl alcohol, iso-butyl alcohol and normal-butyl alcohol, and besides that, esters of some of the higher fatty acids, such as of caprinic, caprylic and capronic acids, and finally we find furfurol and pyridin-like bases. The object of the rectification is to remove, as far as possible, these alcohols, as it is these alcohols that cause us the trouble. These, and the small amount of acid which all alcohol contains, are what we have to contend with in cologne spirits used in the manufacture of perfumes.

The old way of purifying raw alcohol, for making cologne spirits, was, in my opinion, better in some ways and had certain advantages. The alcohol as it was obtained from the first distillation was diluted until it contained about 40-50 per cent of alcohol, and this alcohol was then leached through charcoal, willow or poplar charcoal. It was a systematic leaching through a whole battery of containers filled with charcoal, and in this way the higher alcoholic elements were partially retained and partly oxidized, and the charcoal had also the property of retaining the small amount of essential oil which is contained in every crude alcohol and which is derived from and characteristic of the raw material from which the alcohol is made.

The alcohol obtained by leaching through charcoal was absolutely neutral; it was neutralized by the alkali found in the willow and poplar charcoal, and furthermore, the amount of fusel oil was reduced, being partly absorbed by the charcoal, so that with the following distillation we obtained a remarkably pure alcohol. Of late years it has been found, however, too expensive to use this process, and we find, therefore, in nearly all cologne spirits a small amount of acid.

A process I saw a few years ago in France of purifying alcohol was excellent, but expensive. The alcohol was diluted to about 40 per cent, and heated up in a closed vessel to 60 degrees C., and an absolutely pure petroleum ether was then passed through the alcohol. The process lasted sixty hours, and for each gallon of alcohol they used four gallons of petroleum ether. After that the mixture was allowed to stand to separate, and at the proper time the alcohol drawn off from the bottom, and, finally, distilled. I never saw an alcohol to equal it, but it was very expensive. That process was used in the case of the alcohol supplied to some of the largest and most careful French perfumers, who paid a fancy price for it. A process I have used on a small scale for purifying alcohol, in order to get rid of acid and other impurities, is to add a solution of potassium permanganate to the alcohol. This will oxydize aldehyde, and perhaps to a certain extent the higher alcohols. Then I added lime and let it stand over night, and the next morning I put it in a still and distilled it over the lime. In this way I obtained an alcohol very sweet and absolutely neutral.

Most perfumers have probably had trouble with their metal stoppers corroding, and this is due to the small amount of acid contained even in the best rectified alcohol. This can be avoided if you will go to the trouble and expense of adding lime and distilling your alcohol.

Another point has been brought up—proper storage of alcohol. In the big distilleries after the crude spirit has been rectified, it is put aside in tin-lined copper tanks and stored for one to two years. They are very careful that the tin lining of the tank is perfect, because if it is in the slightest degree defective, and a little of the copper exposed, it is claimed that galvanic action sets in, and the tin will be destroyed, forming a precipitate in the alcohol.

During the time of aging there is an important change taking place in the alcohol. I sent two samples around among the members, one taken from the still a few days ago and the other taken from a container of matured spirits, two years old, and you can smell quite a difference in the two products. If you, perhaps, cannot smell it, it is easy to show it by a chemical test; if you test with a potassium permanganate solution you will find the one taken a few days ago will decolorize the solution of permanganate very quickly, inside of five minutes, and the other requires about a half hour, which shows there is a considerable quantity of impurities in the recently distilled alcohol.

If we consider the alcohols from the various sources of raw material and the best alcohol for the perfumer's use, the majority of perfumers would probably choose wine spirits as the best, and there is no question about wine spirits having a finer bouquet. This is due to the composition of the small amount of fusel oil which it contains. When wine ferments, it is a wild yeast found on the grape causing the fermentation. This wild yeast forms more esters than higher alcohols, and these esters have more pleasant aroma than the fusel oil, as we know it from grain, and especially from potato alcohol. It is, in fact, almost impossible to purify potato alcohol so that perfumers can use it. The amyl and propyl alcohols are predominant, and the small amount of essential oil which I mentioned before being different and characteristic of the raw material, has such a disagreeable character that it is almost impossible to purify this alcohol completely.

The alcohol we obtain from molasses, sugar beets and grains, is very pure. The way the distillation and rectification is carried out nowadays is under such scientific control that the alcohol from these sources really contains less impurities than the ordinary wine spirits. In my opinion, if that is neutralized you will have the best cologne spirits that can be had.

I sent around two small samples of a spirit made by the Amylo process, made in France, and you will see they are different from the samples marked grain alcohol. They are made from grain, but in a different manner from alcohol made by the malt process. You will notice there is quite a difference between the alcohols, and that even the rectified mature Amylo spirits has a different character from the matured spirits made by the malt process.

There is a method similar to the Amylo process called the Taka-Koji process, which Dr. Takamine, of this town, has worked out, and this process gives a very satisfactory product after proper rectifying and aging. The sample I sent around marked "Taka-Koji" is only six or seven months old, and when it is aged for about two years it will give an alcohol that is equal to any alcohol made with the malt process.

RADIATION PYROMETERS.*

The marked development in the construction and use of pyrometers, based on the use of total radiation from hot substances, recently induced the Bureau of Standards to make a study of the subject, as a result of which a report has been prepared by Dr. George K. Burgess, chief metallurgist, and Paul D. Foote, assistant physicist. It embraces a brief account of radiation pyrometry, in which special attention is given to the sources of error including the various factors which influence the indications of radiation pyrometers, the object being to suggest to users various practicable methods of controlling errors and promoting the highest possible accuracy. The investigation has been limited in the main to those types of instruments which are portable and which are in general use as pyrometers, especially in the temperature control of the various processes involved in iron and steel manufacture, alloy foundry work, smelting, steam generation, etc.

The bureau's investigation has demonstrated that when adequately calibrated and correctly used there are available several trustworthy instruments of the radiation type having many advantages in practical use. It has also been made clear that the radiation pyrometer is subject to many influences which seriously limit the accuracy of its readings unless proper precautions are taken. In the use of radiation pyrometers the various sources of error include lag, resistance of thermocouples and variation in resistance with temperature of the source effect of dirt and oxidation upon the condensing device, effect of size of image of source and the temperature of the receiver.

LAG AS A SOURCE OF ERROR.

When a radiation pyrometer is exposed to the radiation from a source at a constant temperature, the pyrometer does not immediately indicate the temperature of the source, but exhibits a certain time lag during which the receiving system is heating up. Eventually the receiver emits or loses by conduction, radiation and convection as much heat as it receives, and a condition of equilibrium is maintained between the source and the receiver. Theoretically this condition is reached only after an infinite time, but it is possible to construct a pyrometer so that for all practical purposes this state of equilibrium is attained within a few seconds, although few pyrometers show such good behavior.

As an illustration of lag effect, the behavior of a Féry pyrometer No. 108, one of the earlier forms of the gold-mirror thermoelectric instruments, may be cited. This pyrometer was sighted into a black body at a temperature of 1335 deg. C. At least 10 min. was required for the instrument to reach this maximum temperature indication. Thus, if the reading had been taken after an exposure of 1 min. to the radiating source, the observed temperature would have been 1300 deg. C., or in error by 35 deg. C. A very much greater error would be incurred for a 30 sec. exposure. A Féry pyrometer No. 109, sighted upon a furnace at a temperature of about 1313 deg. C., showed a maximum reading of 1313 deg. C. in 20 sec. The time required for this pyrometer to reach its maximum indication is satisfactory, but the instrument showed a defect, which is quite common in radiation pyrometers, namely, a rapid decrease in the emf. immediately following the maximum emf. Thus, for an exposure of 20 min. the temperature reading has dropped from 1313 to 1305 deg. C., the real point of equilibrium being reached after 20 min. exposure.

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*From The Iron Age.

It would be possible to calibrate this pyrometer so that the correct temperature would be indicated after 20 min. sighting upon the radiating source. With this particular instrument, however, it is better to make the calibration for general use for a 20 sec. exposure, and, if necessary, corrections may be applied whenever in actual use longer exposures are required.

In general, the Thwing radiation pyrometers are very quick acting because of the simple type of receiver employed. The Féry pyrometers are complicated by the focusing device. These mirrors, which are very essential for the convenience of focusing and operation, may cause considerable trouble. No generalizations can be drawn as to the magnitude of the lag for the various types of pyrometers. Apparently no two pyrometers of the same type are constructed exactly alike. If a radiation pyrometer is to be used for highly accurate work, the effect of lag should be thoroughly examined, so that the calibration and all readings may be made with an exposure for which the change of lag with time is a minimum.

RESISTANCE OF THERMOCOUPLES AND ITS VARIATION.

If the radiation pyrometer is to be used with a galvanometer it is desirable that both the resistance of the thermocouple and its variation in resistance with the temperature of the source be small. These conditions are well satisfied by all the radiation pyrometers examined. The emf. developed by the thermocouple on open circuit when the pyrometer was sighted upon the furnace at any definite temperature, and the potential drop across the resistance connected to the couple terminals, were measured by a potentiometer.

The resistance of the couples of Féry mirror pyrometer No. 111, Thwing cone pyrometer No. 120, and a Brown pyrometer were found to be about 0.8, 0.6 and 0.2 ohms respectively, with variations from these values of 2 to 3 per cent for a range in temperature of the source of 500 to 1200 deg. C.

EFFECT OF DIRT AND OXIDATION ON THE CONDENSING DEVICE.

Whipple has observed that a slight film of oxide on the surface of the concave gold mirror of the Féry or Foster radiation pyrometers does not seriously alter the amount of radiation reflected (9.6 per cent), as the greater part of the energy exists in the form of long wave lengths, which the tarnished mirrors reflect without difficulty. This statement has frequently been interpreted to mean that in spite of dirt accumulation, stains and scratches, the gold surface remains unchanged in its reflecting power, but obviously such constancy is not the case. Pyrometers subjected to severe use in steel mills and other industries soon become coated with dust and dirt.

To ascertain the errors to be expected from this source an experiment was made with a Féry mirror thermoelectric pyrometer No. 108, which was calibrated first in the condition received and, second, after the accumulation of dirt had been removed from the mirror. The case was not exceptional, as many other instruments have been received which were just as dirty. The difference in calibration with clean and with dirty mirrors varied from 100 to 160 deg. C. in the temperature range 600 to 2000 deg. C. Since the ordinary calibration of the pyrometer is made with clean mirrors, the instrument as used with dirty mirrors may read too low by over 100 deg. C.

The effect of dirt upon the surface of the aluminum cone of the Thwing pyrometer has not been tested, but without doubt the calibration would be altered in a manner quite similar to that observed in the case of the Féry pyrometer.

EFFECT OF DISTANCE AND SIZE OF SOURCE.

The simple geometrical optics of a radiation pyrometer indicates that the readings should be independent of the distance from the pyrometer to the radiating source, provided the uniform source were of sufficient size required by the constant aperture of the instrument. Enlarging the size of the source above this limiting value should produce no effect. Actually this ideal condition by no means obtains, and herein lies the most serious error to which radiation pyrometers are subject.

The causes for the dependence of the readings of a radiation pyrometer upon the distance from the instrument to the radiating source are two in number, (1) atmospheric absorption and (2) construction of the pyrometer. The errors due to atmospheric absorption are small in comparison with those occasioned by an unsatisfactory construction of the pyrometer. The effect of atmospheric absorption is to diminish the reading of the pyrometer as the distance to the source is increased.

THE TEMPERATURE OF THE RECEIVER.

It is usually assumed that the temperature of the hot junction of the thermocouple does not vary much from that of the room in which it is used. This assumption is approximately true in the case of some pyrometers; for example, the Thwing; but with certain Féry instruments this temperature may rise very considerably. The temperature of the cold junction of the thermocouple receiver is, in general, closely that of the room, and should change very little. Hence, if the temperature-emf. relation to the thermocouple is known, the temperature of the hot junction or receiver for any furnace temperature may be determined from the emf. developed.

The errors in calibration of a pyrometer as a result of entirely neglecting the temperature of the hot junction of the thermocouple are small, only a few degrees at the most in the range from 500 to 1500 deg. C. The question has been considered here mainly because of the general impression that the effect of the temperature of the hot junction of the thermocouple must necessarily rapidly decrease with increasing furnace temperature.

The Bureau receives a large number of pyrometers, for test and standardization, from various technical industries located throughout the country. Heretofore this testing required about three days for a single instrument on account of the difficulty in heating a furnace to an exactly uniform temperature. A new method has now been developed which permits a satisfactory standardization of a radiation pyrometer within one hour.

REQUIREMENTS FOR LEDGER AND BOND PAPERS.*

By HARRY A. MADDOX.

Ledger paper ranks among the most important products of the papermaker and the case of the finest grades represents one of the most remarkable achievements in the world of paper. The importance of the stock makes it necessary to devote persistent consideration to the principles which must always guide its manufacture. To this end, therefore, the following matter will purport.

The essential factors are durability of material and physical character, the latter including ink resistance, erasure, surface color, strength, finish, etc. Sundry other features of only slightly less importance are the watermark, sorting, counting, packing, etc.

The development of loose-leaf ledger systems has created a distinct incentive for new ideas in papermaking, mainly in the direction of strength, color, texture, and character of wiremark. It has become realized more and more that strength to an extreme degree, combined with the maximum of durability, is an absolutely essential feature in ledger paper of grade number one. Formerly, almost every type of ledger paper was run under a laid dandy, a matter for which no efficient reason can be assigned. Wove papers are more suitable in every way for ledger stock and it may be desirable to devote a little consideration to this phase of our subject.

In the first place, wove texture presents an improved appearance; it also introduces an equally distributed and improved strength by reason of the absence of the thin ridges which are characteristic of the laid mark. The laid wire dandy imparts what is really a watermark, consisting of thinned and thickened portions in the paper. In testing a paper for strength it is an axiom that watermark portions must be avoided, but on a laid paper it is manifestly impossible to avoid the markings. The maximum of strength from the same stuff is secured by running the wove dandy. Continuing further, it may be said that the surface of wove paper presents a more even and responsive pen-writing area than if it were undulating with laid marks. Certainly it presents a much better opportunity for unbroken ruling and printing, as any practical stationer will readily admit. Add to this that the wove dandy closes the web better, thus enabling a closer texture to be obtained, and it would appear that we have sufficient reason for a further development in the use of the wove dandy on ledger and account book stock.

Watermarking is a branch of the art of papermaking which has not received sufficient attention from a commonsense point of view. Massive marks, embodying incongruous devices and lettering of unwieldy proportions, have almost become established, to the detriment of the paper itself. It is perhaps advisable under these conditions to consider the true purpose of a watermark. In the first place it is a brand of quality; secondly, it is an advertising agent whose purpose is to secure repeat and enhanced orders for the same quality. Certain types of standard watermark are applied to the several sizes of account book paper as a derivation from old customs. Although this habit i on the wane, it is still largely practiced, particularly on English papers. In a sense the marks are useful, but not sufficiently so to counteract their disadvantages. To the papermaker or the user of the ultimate book they are of no earthly use or value, while if the stationer knows his business there is no necessity to point out the size of a sheet by means of an incongruous traditionary service. The present position of the watermark, with few exceptions, is the center of the sheets. In our opinion that position is ugly and useless; further, it is a distinct hindrance to the paper ruler, while the argument may also be put forward that it weakens the sheet to an appreciably extent.

A watermark will serve its purpose equally well, better in fact, by being small; certainly also it will aid toward uniformity and beauty in the sheet. The first essential, then, toward successful and up-to-date watermarking is that the device or name, or both, should be small. At the same time it should also be distinct, preferably of the fine outline variety. Having attained the desired diminution in size, we may next proceed to a perusal of position. The worst place for the watermark is along the middle of the sheet, yet as we have already observed that is precisely where most of them appear.

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*From Pulp and Paper Magazine.

A short examination of the watermarks in written-up account books or in printed volumes will conclusively prove the extreme difficulty which attends the effort to decipher a large watermark in this position. All ruled and printed books have a wider margin of blank space at the foot than elsewhere. This in itself points the way to correct apposition of the watermark. It may run twice along the foot in order to fall on every leaf or folio. The small amount of trimming which accompanies the manufacture of standard size account books could be readily allowed for. Coincident with this approved position of the mark, the work of the ruler and printer is aided considerably and better results are assured. A deeply impressed device in the middle of a sheet will hopelessly break up the contour of either a fine-ruled or printed line. It should be borne in mind by the papermaker that the ruler's pens ride very delicately over the surface of the sheets, therefore at every depression a broken line is inevitable.

While on the subject of watermarks a word or two may profitably be said concerning wiremarks. These refer to the wire pores so common on the underside of both wove and laid machine papers. At all costs these should be eliminated on high grade ledger stock. It is a common complaint of the ledger clerk that he encounters considerable difficulty in writing on the wrong side of the paper. It is vastly annoying, after running smoothly over a full page, to turn over leaf and engage a page exhibiting a distinctly different character to the first. Much may be done during manufacture to eliminate wire pores. In the first place, the pulp should be well beaten; then avoid an unduly severe wire shake at the wet end. Work a suction couch roll if possible, or at least control the style of jacket and amount of pressure to reduce the danger of maintaining a wiremark.

The web must not bear any trace of the wire pattern after passing the press rolls, for little help can be expected at the finishing end; in fact, the damping and tub-sizing are more likely to open out the mesh than otherwise. Naturally, we do not expect nor desire to remove the appearance of a woven wire so far as the look-through of the paper is concerned; our remarks apply merely to the porous state of the wire side of many makes of ledger paper.

The question of even-sidedness in color is vitally combined with the foregoing proposition of eliminating wiremarks, for the treatment that rids the latter perfects the former. In the control of color in ledger stock, among others, two things need to be considered, the specific gravity of the color and the influence of suction on the web. Smalts is a notably heavy mineral color, with ultramarine a distant second. Papers dyed with smalts are notable for the dark color of the underside, particularly in the case of hand-mades. There is neither use nor beauty in a ledger paper which approximates to a duplex tinted in the matter of coloring. So far as possible this effect must be overcome.

Much may be done by using well beaten pulp, which settles slowly on the wire and retains the color well on the surface. At the same time it is of no use to employ correctly beaten stuff unless it is kept well mixed in the stuff-chest and en route to machine. A good mixing device which will keep the particles of colors in adequate suspension is a necessity where smalts and ultramarine constitute the dye. At the wire, the water must be allowed to carry on for a sufficient distance in order to impart strength and a slow and steady settling. The suction rolls and pumps must work lightly to accommodate this process, as a big pull at the suction boxes irretrievably sets the wiremark and draws the color to the underside.

With the attainment of even-sidedness in coloring, there still remains much to be said. The type of dyestuff used for toning any particular grade of azure or blue stock is an item of information usually known only to the papermaker himself or the chemist who decides to make an analysis. It would be a decided advantage to the stationery trade and to particular users if the grade or type of dyestuff were denoted on the stock wrapper or on the sample sets. It is often important that paper for certain purposes must be dyed with a material immune from attack. For example, paper for permanent record journals which would require to be stored or used in an acid atmosphere would not be satisfactory if dyed with second-rate ultramarine. Under present conditions, neither the stationer nor his client is aware of the nature of the dye with which the stock is colored. As a consequence, it is only when the damage is done that the importance of determining the dye is recognized. Some rules should be defined by papermakers and buyers with a view to setting down regulating standards for ledger papers.

We would suggest that for grade I, papers suitable for permanent records, state documents and forms, books, etc., and for blued stock, that must be fast to every likely atmospheric reagent, smalts alone should be used and that only of the best quality. Every precaution should be taken to prevent a speckled appearance due to the many gritty and oversized particles characteristic of poor grades of smalts.

For grade II, books of secondary importance and those not likely to encounter severe fumes, an almost permanent coloring would be assured by using a mixture of smalts and ultramarine of good quality.

For grade III, where absolute fastness may be subservient to brilliance of tone, pure ultramarine alone will provide everything desirable. Such a paper should be absolutely free from acid traces and contain but the minimum of alum, whether from the preliminary resin or ultimate tub size.

Smalts is an unfading blue of low tining power and embodies in its composition silica, potassium, and cobalt glass, or chemically as a potassic cobalt silicate.

Smalts may embody up to 67 per cent of silica, whereas ultramarine does not hold above 42 per cent in the best grades.

Ultramarine is a double silicate of aluminum and sodium, together with bisulphide of sodium. The best grades are rich in silica and the value of the color for fastness may be judged partly by this content. During manufacture, and especially at the drying end, ultramarine is submissive to the effect of alum embodied in the pulp, but the interaction practically ceases when the paper is closely packed and not exposed to light, heat, or damp, provided that there is not present a considerable excess of alum or acidity. In the drying process, air or loft-drying methods provide much less likelihood of deterioration in color, a disaster which is often due to sudden and strong heating at the cylinders.

To briefly restate the case, smalts should be used for highest grades of permanent ledger paper as also for important records in chemical manufactories, and other places where fumes are prevalent. Ultramarine would soon display its susceptibility to acid fumes and would in time totally disappear. The reasoning of permanent color applies with equal force to the choice of ruling, printing, and writing inks, perhaps even more vitally than to the paper dyestuff, for bleaching or fading of the latter would not be likely to affect the written or printed record. It may be presumed, however, that the effect of the action carried on *in situ* during the progress of color deterioration might influence the character of the paper itself in some degree

Where there is no probability of destructive chemical influence on the paper, as in professional offices, ultramarine or indanthrene coloring would be efficient, but the former is preferable by virtue of the purer tone of color imparted.

CAMPHOR FROM SHRUBS.

The Bureau of Science of the Philippine government is making a study of the plant known as *Blumea balsamifera,* known by the natives in the Philippines as "sambon" or "gabuen," and which produces camphor. The shrub is one of the most common weeds in the Philippines. It grows from 5 to 8 feet high, with a stem almost woody in texture, and has long been used by the natives of the Philippines as well as by natives of China for medicinal purposes. The Chinese in parts of Kwantung and Kwangsi Provinces already distill considerable camphor from the plant, the chief drawback to the more extensive use of it being the amount of labor required to secure the gum. It is well to note in this connection that the Bureau of Forestry at Manila is introducing the ordinary camphor tree of China and Japan into the mountain districts of Luzon in large numbers for the purpose of building up future camphor production in the islands.

SELECTING REFRACTORIES FOR THE FOUNDRY.*

BY WALTER H. KELLEY.†

Every superintendent of a foundry insists on knowing the analysis of the coal he is using, while but few investigate the analysis and physical characteristics of their fire brick and fire clay requirements. All fire clay brick are essentially silicates of alumina and expressed in the lowest terms are composed of the two varieties of clay, namely, the hard, flint or block clay, as it is often termed, which forms the real body of the heat-resisting material, and the soft or plastic clay, acting as a bond to give physical strength to the brick. As conditions may warrant a larger or smaller portion of the hard clay may be calcined previous to its manufacture into brick. Upon the character of these clays, the fineness to which they are ground and the degree of burn given them, depends the character of the brick. In general, a fine ground, hard burned brick gives superior results in the side walls and a more porous, open, and if we may term it, "elastic" brick does better in arch work. There is here given a fairly representative analysis of a high grade Pennsylvania fire clay brick, cited as being merely typical.

	Per cent.
SiO_2	52.93
Al_2O_3	42.69
Fe_2O_3	1.98
CaO	.33
MgO	.38
Alkalies	1.55

It has been demonstrated, other things being equal, that as the percentage of silica increases in a fire brick, the refractoriness decreases, the excess of silica being in a free state and uniting with such impurities as may be present, lowering the fusion point of the brick. The theoretically perfect fire clay, a true silicate of alumina, will show in accordance with the oxygen ratio the following: Alumina, 53.27 per cent and silica, 46.73 per cent. Such a pure silicate of alumina does not, of course, occur in nature, but as a general rule, the nearer the silica and alumina are to these proportions, the more refractory is the material.

Analyses of fire brick taken from various foundries where trouble has been encountered have shown from 59 to 73 per cent of silica, or an even higher percentage. Of the majority of clays used in foundries such analysis indicates that they are made from so-called top vein clays, lying above the coal measures, and such as are more commonly used in the manufacture of sewer pipe, building brick or fireproof material.

Nevertheless analysis alone does not tell the story as to how any given clay or brick will work out in your furnaces, in the side walls, for instance, where it encounters high temperatures, the scorifying action of the slag and cinder and the wear and tear of the slice bar or poker. Nor will it tell the results in the arch, often subjected to the most intense heats, with forced or induced draft, with mechanically fired furnaces and with fuels of various kinds.

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*From the Iron Age; an abstract of a paper presented Sept. 8 to the American Foundrymen's Association, Chicago.

†Harbison-Walker Refractories Company, Pittsburgh.

The physical structure of the brick should also be considered in making decision as to its selection. Where bituminous coal is used as the fuel, it has been found that a hard dense brick of higher refractoriness gives the best results in the sidewalls, especially along the clinker line. The importance of using a brick of the proper physical and mechanical composition in side-walls has brought about the introduction of bauxite for this portion of the furnace construction. While they have not as yet probably been given an adequate test, their adoption bids fair to later become a factor in the selection of the material used in lining at least portions of the several different kinds of furnaces in your equipment. It will be dwelt upon more fully later.

Ordinarily a brick used in the arches should be of not too hard a burn and of a comparatively coarse grind, as a brick of this kind will better withstand the sudden changes of temperature encountered. There are, of course, variations to this rule, as with the use of anthracite coal with blast or forced draft, where the physical structure of the brick should be dense and hard to better withstand the cutting action of the fast-moving gases of combustion.

Care should be exercised in selecting a fire clay for laying up the brick-work of a refractoriness corresponding with the brick. When a manufacturer of a high-grade brick begins to insist that it should be laid up with a clay corresponding in refractoriness his motives are not invariably looked upon as altruistic, but it is a common error to use so low a grade of clay that its plasticity must be reduced by the mixture of sand to give a sufficient sharpness to work the material. In such a case the joints may often melt and run out while the brick themselves would be unaffected. Any addition of lime, mortar or cement should be avoided, not so much because of the injury done by a very small percentage of this material, as because of the fact that any given percentage is in practical working very often doubled or trippled, due to carelessness in proportioning the mixture.

Air furnaces are particularly severe on fire brick. This is due not so much to the high heats attained, as to the intermittent operation of this type of furnace. The highest grade of fire brick obtained is none too good and care should be exercised in the selection of brick of the proper burn to withstand the variable conditions occurring during the operation of the furnaces.

Hard-burned and fine-ground brick should be used in the side-walls of these furnaces to better withstand the impinging effect of the flames against the walls, deflected, as they are, from the stock which, when originally charged, is very bulky and takes up considerable of the space of the melting zone. Medium-burned and coarse-ground brick should be used in the roofs to overcome spalling and to withstand the variable temperatures naturally occurring.

Considerable of the difficulties with the clinker of the fuel bed adhering to the side-walls of the combustion chamber have been overcome by the use of a steam-pressed brick along this clinker line. The use of bauxite brick and steam pressed brick has also overcome to a very considerable extent the scorifying action of the slag of the bath upon the side-walls of the melting zone.

The side-walls of this type of furnace have to be repaired very often, due to the action of the slag of the bath cutting out the brick-work wherever it touches and thus undermining the upper portion of the walls.

As the temperatures employed in annealing furnaces will vary from only 1,000 to 1,500° or possibly a little higher, a second quality brick is used almost entirely throughout excepting in furnaces of great width and where the flame of combustion has to carry a considerable distance. Here it has become necessary to use a first quality brick in the fire boxes of those that are coal fired on account of the higher temperatures necessary to carry the heat across the furnace.

The best practice is to install the bottom of these furnaces with tile 12 in. in width and 5 in. thick, varying in length from 12 to 18 in. These tile are made as tough and dense as it is practical to make them, so that they will stand the wear and abrasion encountered in the charging of the furnace. As each of these blocks covers a larger area than a standard size 9-in. brick, they afford a more even surface and considerably reduce the number of joints in the brick-work of the bottoms.

In brass melting furnaces of the pit type wherever a crucible is used and where coke or oil is ordinarily the fuel, a highly refractory brick of medium coarse grind and of a good strong burn give the best results. A brick with these characteristics will better resist the action of the fused coke and the deposits from the oil.

In the tilting melting type of furnace the most refractory fire clay brick obtainable is required to secure good results. The brick should be of dense structure and of hard burn to resist the action of the oil and air which are admitted usually under the very heavy pressure. The slags created are very scouring in their action and consequently do not permit of the use of an open or coarse grained brick. Specially shaped brick are usually required to line this type of furnace, to overcome the number of joints occurring when lined with standard brick. A good many of the above furnaces are lined with ganister, which makes a very satisfactory lining material as it can be repaired very handily.

In steel converters the lining most generally used is silica brick, while there are a number lined with ganister, which is a mixture of practically pure silica grits and a refractory clay, which is rammed around wooden forms. Many of these converters are first lined with silica brick, to the surface of which is then added a coating of about 3 ins. of ganister. I know of some converter linings thus installed that have given over 18 months' service.

In crucible steel melting furnaces which are usually of the regenerative type, the use of silica brick is rapidly replacing clay brick in the lining of the melting zone. Where formerly there was obtained about four to six months' service with the clay brick lined furnaces, we have records of furnaces lined with silica brick giving a life of from 36 to 45 months, the average life of these furnaces today is from 14 to 18 months.

Brick to be used in cupolas should be dense, hard, tough and very refractory. Blocks for lining around the bottom of the cupola and for a distance of 4 ft. or so above the tuyeres should be made of flint clay high in alumina, with sufficient bond clay to make the brick strong and tough. The manipulation of the clay and the mix, grind and burn have to be carefully considered to secure the maximum heat resisting capacity, together with ability to stand the cutting action of the blast and the wash of metal and slag. From a distance of about 2 ft. above the tuyeres to the charging doors the blocks should be made to withstand abrasion, as well as heat and they should be exceedingly dense, hard and strong.

In the electric furnaces silica brick are used entirely, excepting where basic steel is produced; the latter requires that the bottom and side-walls be constructed with magnesia brick to withstand the action of the basic materials charged into furnace. It is surprising how well these brick have withstood the severe treatment given them in this type of furnace. While we all appreciate that silica and magnesia brick will spall severely when subjected to sudden changes of temperatures and fully realizing the intermittent operation of these furnaces, still we would not consider any other refractory material than silica or magnesia brick to withstand the high temperatures occurring therein.

The life of the lining of an electric furnace is at the best a very short one and considerable of the difficulty with the short life of these linings is due to a very considerable extent to the unnecessarily high temperatures often attained. While they have all sorts of devices for registering the voltage and amperes required during the melting of a charge, there is very little attention given to the temperatures attained. In fact, there is no instrument that can be depended upon to record accurately the high temperatures that no doubt are often attained during the operation of the furnaces. I have heard operators of these furnaces state that they judge the working temperature to be slightly over 1,900° C. This would mean a temperature of about 120° Fahr. beyond the fusion point of the brick. I have seen the original lining of an electric furnace run for 48 consecutive days and the four or five subsequent linings would last from five to ten days.

Regarding malleable furnaces this practice is about the most severe of any on fire brick. The life of these furnaces is referred to in the number of heats and not days or weeks, and is governed by the service obtained from the brick in the side-walls, as the roof sections or bungs are often renewed during the operation of the furnace.

Fine ground and hard burned brick should be used in that portion of the side-walls as high up as the slag line reaches. Hard burned and highly refractory brick should be used in the balance of the side-walls to resist the impinging effect of the gases of combustion and coarse ground and light burned brick should be used in the bungs to better withstand the variable temperatures naturally occurring in this practice where coal is the fuel most generally used.

A NEW FORM OF EVAPORATOR AND DRYER.*

By L. BALDERSTON.

Before describing the modified form of apparatus which is the subject of this note, it may not be amiss to review the conditions which a satisfactory evaporator and dryer should fulfill. The plate on which the dishes are set must be horizontal, and of heavy enough material not to sag in the middle with use, in order that the film of material left in the bottom on evaporation may be of uniform thickness and so dry evenly. The cover must fit neatly so that there will be as little flow of air as possible along the plate on which the dishes rest, as this would prevent those near the edge from reaching the desired temperature. There must be a sufficient but not too large flow of air through the confined space, in order that the water of evaporation may be carried off without cooling the interior below 95 or 97° C. This air supply must enter all around the walls at a height above the base plate a little greater than the height of the dishes and pass out at the top. There must be a free flow of steam through the double-walled cover, giving in the neighborhood of one gallon of water of condensation per hour from an apparatus 30 ins. square. The constant level apparatus, which should be not less than 2 ins. in diameter, should communicate with the boiler near the bottom, and be adjusted so as to keep about 4 ins. of water in a boiler 6 ins. deep. The cover should be so arranged as to be easily raised without disturbing any connections. The apparatus should be of copper throughout. If the joints are made by soldering, they will inevitably become leaky after prolonged use, as the solder corrodes under the continued attack of steam, when in contact with copper. The seams should therefore be brazed together. The construction of the cover should be as simple as is consistent with efficiency, so as to save expense. The flow of steam from the boiler to the cover is usually provided for by two tapered ground joints of brass with about 1 in. opening, one on each side. These joints do not need to be very perfect, as the film of water which forms in them between the brass surfaces suffices in the absence of pressure to make a good seal.

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*From the Journal of the Leather Chemists' Association.

It is customary to connect the apparatus with a condenser so that it may furnish a supply of distilled water. Where a number of "ovens" are used in one laboratory, it is convenient to have them connected to one condenser, instead of putting a condenser for each on the cover. In the form of oven commonly used, the steam escapes from the cover at the top, the cover being shaped like a pyramid. Where several are connected to one condenser, it is necessary to disconnect the steam escape in order to lift the cover, or else to use some sort of more or less complicated flexible pipe for the steam. Where each oven has its condenser fastened to its cover, the weight to be lifted is considerable, and rubber hose connections are necessary for the water to and from the condenser, requiring to be looked after quite frequently.

In this laboratory eight ovens are in use, and the matter of leaks above referred to is a constant source of annoyance. The hinges by which the covers are attached are also held with solder, and they often come loose. Beside, the disconnecting and connecting of the steam escape is troublesome.

As W. K. Alsop and I went over the matter of possible improvements, it occurred to us that there is no necessity to take the steam out at the top. The ordinary form of steam radiator for heating purposes has but one opening, at which the steam enters and the water of condensation escapes. We decided to try taking the steam out at the hinge. It might seem that in such a case not all parts of the cover would be heated equally. We reasoned that if there is an abundant steam supply, if any part of the cover tended to become cool, condensation there would make a partial vacuum, and more steam would flow to that spot. An old oven was accordingly fitted up as follows: the hinges were taken off and replaced by a piece of inch brass pipe extending all the way across the back at the bottom and projecting several inches at each end. Openings from the inside of the hollow cover into this pipe were provided, so that the escape of the steam and water of condensation could take place through the pipe, which is sealed at one end, and connects at the other with a suitable condenser. The projecting ends of the pipe rest in supports fastened to the boiler, so that the pipe acts as a hinge and as the joint connecting it with the condenser is loose, the cover may be raised without disturbing anything. The arrangement works perfectly, the space inside being heated quite as fully and uniformly as in the other ovens from which the steam escapes at the top.

The next point which claimed attention was the matter of reducing cost by simplifying the shape of the cover. Since the steam was not to escape at the top, a pyramidal shape was not necessary, and if the roof of the cover were close enough to the dishes, the whole enclosed space could be kept hot without making the side walls double. To test this reasoning, a cover was made whose roof has a double slope like that of an ordinary house, rising 4 inches from edge to ridge on an oven 24 inches wide. The gable ends and front edge are of one thickness of metal, the back vertical wall being double as usual, to provide connection with the pipe hinge. Steam enters at each end of the top angle of the roof. The water of condensation from the front slope of the roof flows through a small pipe at the side to the bottom of the back. In the oven room of this laboratory, where the temperature during the night is about 110 degrees F. this arrangement works very well. We think, however, that it will be well to line the single walls with asbestos paper. We were fearful that the height of the roof being so small there would not be a sufficient draft created to make a good flow of air. Four pieces of inch pipe equally spaced along the ridge, opening out from the covered space and rising 8 ins. above the top provide as much draft as the ordinary form of oven. The air inlets are larger and less numerous than usual, ½ inch in diameter and four on a side. It will be easily understood that this form of cover is very much simpler and less expensive to make than one which is double-walled throughout, and pyramidal in shape.

Testing and Properties of Textile Materials.

The Bureau of Standards Circular No. 41, relating to the testing and properties of textile materials, has recently been revised and enlarged. Several changes in wording have been made to eliminate misunderstandings that have occasionally occurred. Other changes have been necessitated by the adoption of new and improved methods of testing, all of which are explained in some detail. Several photographs and diagrams have been added to assist in describing the apparatus used. The new circular contains a general consideration of the procedure used in testing textile samples submitted in connection with purchases by the various departments of the Government. These samples include raw fibers, rope, twine, thread, yarn, and all kinds of fabric. A large amount of such materials is purchased annually by the Government, and it is therefore necessary to use great care that the proper value is obtained. Besides the work done for the Government, the Bureau of Standards does testing for private persons in cases of dispute or when proper facilities are not available elsewhere. For the information of those interested, a schedule of fees has been included in the circular, thus enabling those who will need to have tests made by the bureau to estimate the probable cost. Work is often done free of charge when the bureau considers it to be of such a nature that it will give information valuable to the bureau in solving some of its scientific and practical problems.

PAPER.*

For many years efforts have been made to replace by pulp and paper many materials which in various ways serve a special purpose, and very good results have been attained. In the field of electricity, for instance, mica and other nonconducting substances were used for insulating material. We now find insulating paper most used for this purpose as it fills the requirements and is cheaper than other materials. The insulation must not only be made up of a nonconducting substance but must also be free from substances that even in small amounts are conductors of electricity or are capable of becoming so under certain conditions.

Every plant fiber in the form of paper or press board has the property, when dry, of insulating. On this account one need not be very particular in the choice of raw material for this purpose, but must take great care that the pulp is so prepared that a sheet can be easily made which is well closed, hard, and equally thick at all points. It is these properties which are increased by careful beating, operation of the machine, pressing, finishing, etc., more than by the choice of raw material, though some materials are much more easily worked up than others.

A good, reasonably cheap, satisfactory insulating paper can be made, according to *Pappen und Holzstoff Zeitung*, 44, 1914, of raw material comprising as much as 75 per cent old paper. The rest may be jute, spinning waste, or even cheap rags. Paper shavings containing wood or free from wood are applicable. In regard to the working of old paper it should be noted that this must be done cold. Hard material is first softened cold and may be treated in the kollergang or be shredded. The latter is recommended here because the fibers are less injured and are well separated, while in the kollergang, unless great care is taken, the stuff is ground too short, i. e., beaten "dead." If softened or beaten warm, the old paper loses "rattle" and "handle," losing in this way too much sizing, hydrated fibers (slow stuff), and a certain amount of fiber, the product showing a lack of "handle" and a very poor "rattle."

Jute, bast fibers, or rags are prepared by beating the uncooked stuff to halfstuff in a breaker. This is beaten in the holländer to whole stuff and the old paper mixed in at the same time. The materials are well mixed together for twenty or thirty minutes, then beaten as long again with the roll lowered. This time can be shortened or lengthened according to the size and capacity of the beater and the kind of bars and bed plate. It is always essential that the stuff have a good greasy feel, thus assuring a well closed, dense sheet. To get this result the beater is furnished fairly thick and the roll and bed plate should have broad, dull bars. The roll must be heavy so as to get the stuff more greasy. All addition of materials must be avoided, sizing may also be omitted, as with a good smeary pulp and proper formation of the sheet the paper will be sufficiently sizefast without it. For a specially ordered hard product a little rosin would help.

Color can be added as desired, usually a bright to a dark brown, as in leather board. Suitable aniline colors are used for this purpose. The addition of earths must be avoided because all minerals are more or less hygroscopic and some eargerly absorb moisture from the air or other water directly. Water and moist substances are fairly good conductors of electricity and would make the paper or board unfit for insulating purposes.

On the board machine care should be taken that on a single cylinder machine the removal of water occurs mostly at the forming roll, because here in its formation the sheet is repeatedly pressed and so made dense and well closed. An important rule for this machine is that the stuff in the cylinder vat be kept thin so that the felt takes off thin layers and the cylinder always takes up a very uniform and thin layer of stuff. In order to keep the concentration in the vat constant, the agitator should be at the bottom and should be kept in perfect condition. There should be no unnecessary agitation, or the stuff will be sent first to one side and then to the other, making much of the board of unequal thickness.

In order that the thin layer of stuff on the cylinder be not too much dewatered by the felt, it is necessary in the manufacture of insulating board that the couch roll rest rather high on the crown of the cylinder. The felt must be thick and at the same time permeable so that the sheet reaches the couch roll with the necessary amount of moisture. If layers are too dry they will not press together but the board will split when dry.

The couch roll is heavily weighted and of metal. Wood rolls are obsolete, produce much waste, and give a board of unequal thickness with knot and crack mark.

Between press plates of metal in a hydraulic or other powerful press the board is further dewatered by strong pressing. Small packs are used as otherwise the pressure is too elastic and weak. The pressing must be carefully done, as a sheet otherwise satisfactory may be spoiled in this operation. The press smooths out slight unevenness in the thickness, makes the sheet firm and dense, gives it a glaze, and assists in the drying.

Because each sheet must have a uniform thickness, and one sheet be as thick as another, it is recommended that such a thickness indicator as the recently-invented Schopper-Metaschk apparatus be used. This instrument works continuously and measures to 1/100 millimeter.

The complete drying of the board is best accomplished in passages. These provide a very uniform drying, with the least injury to the goods, the least waviness, and with no waste formed.

After subsequent damping in a closed humidifier, the board can be glazed without further treatment, for each sheet is finished with a very high glaze.

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*From Paper.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

San Francisco Meeting of American Electrochemical Society.

The September meeting of the American Electrochemical Society will be held in San Francisco, from Thursday, Sept. 16th, to Saturday, Sept. 18th. Special transportation facilities have been arranged for by a committee of which Mr. J. M. Muir, 239 West 39th street, New York, is chairman. Various routings are offered and full particulars can be obtained by addressing Mr. Muir. The regular society train will leave New York on Saturday, Sept. 11th, and the special engineers' train on Thursday, Sept. 9th.

At the time of holding the meetings, the American Institute of Mining Engineers and the American Institute of Electrical Engineers will also be in session, and joint meetings have been arranged with these societies for Friday, Sept. 17th. During the following week the International Engineering Congress will hold its meetings.

The following list of papers have been accepted to date and will be presented by members of the society at the time specified below:

THURSDAY, SEPT. 16TH: Regular meeting of the American Electrochemical Society.

W. D. Bancroft: "The Peptonization of Chromium Oxide." Dealing with the clearing up of solutions of chromium oxide by the action of certain chemicals which de-coagulate the solution.

F. M. Frederiksen: "Electrochemical Synthesis of Phenol Hydroxyl Amine." An application of electrochemistry to the production of an organic chemical.

A. G. Betts: "Electrolytic Antimony Refining." Record of experiments to refine commercially impure antimony, by the use of various solutions and varying current densities.

C. W. Bennett, Rose and Tinkler: "Electrodeposition of Nickel." Discussion of the conditions of depositing adherent nickel plating, and the use of rotating cathodes in the operation.

W. D. Bancroft: "Electromotive Forces." A review of the fundamental formulae of electromotive force and amendment of the fundamental Nernst equation, deriving it also from a more general standpoint.

Wills and Schuyler: "Heat Losses from an Electric Steel Furnace." An investigation of the heat losses by gases issuing from the doors, by water cooling of the electrode collars, and by transmission through the electrodes.

W. R. Mott: "Use of the Flame Arc in Paint and Dye Testing." An extended investigation of the light value of the white flame arc, arrangements for testing paints and dyes therewith, and results obtained.

R. S. Bosworth: "Collection of Radium Emanation and Its Application for Therapeutic Use." A short review of the modern hospital practice of collecting emanation and applying it.

F. T. Snyder: "Electric Steel Costs." An analysis of the cost of making steel from cold raw materials on a small scale for foundry use.

FRIDAY MORNING: Joint session with the American Institute of Mining Engineers. The papers to be presented by the A. E. S. will be of mutual interest to both societies.

R. S. Wile: "Melting of Ferro Alloys in the Electric Furnace." A discussion of the economy in steel making practice of melting ferro alloys, particularly ferro manganese, in electric furnaces and adding them melted to the steel.

L. Addicks: "The Electrolysis of Copper Sulphate Liquors Using Carbon Anodes." An extended account of recent experiments in leaching copper ores in Arizona, and of the successful use of carbon anodes in electrolyzing sulphate solutions.

F. R. Pyne: "Solution Stratification as an Aid to the Purification of Electrolytes." Description of a new method of withdrawing liquor low in carbon from the regular refining baths, by various outlets properly placed, using the principle of stratification.

Other papers will be presented by members of the American Institute of Mining Engineers.

Friday Afternoon: Joint session with the American Institute of Electrical Engineers. The papers to be presented will be of mutual interest to both societies.

F. M. Sebast: "Electrical Resistance of Copper-Nickel-Chromium Alloys." Records an investigation of the resistances of alloys of copper with chromium, alloys of nickel with chromium, and ternary alloys of the three metals.

J. W. Beckman: "Electrochemical Possibilities on the Pacific Coast." A complete discussion of the location and cost of power supply of raw materials and possible markets for electrochemical products manufactured on the Pacific Coast.

Saturday: Special arrangements have been made for members to visit mining, metallurgical, hydroelectric and various other engineering operations in California.

Russian Market for Chemicals.

The U. S. Consul at Moscow reports that serious difficulties are being experienced on the market for chemical goods in consequence of the absence of supplies. Great quantities have been purchased in the United States, England, and other countries which can not reach Moscow. According to the Moscow Exchange, the present prices on certain chemical goods are as follows: Russian borax in crystals, \$14.26 per 100 pounds; Russian yellow wax, \$59.89 per 100 pounds; Russian white wax, \$62.74 per 100 pounds. The Moscow diocese had decided to purchase abroad the required quantity of wax, and had sent a delegate to Portugal and other countries to make direct purchases. But the purchased supplies have not arrived, and the diocese is threatened with a shortage of material for manufacturing wax candles. American resin is sold at \$8.56 per 100 pounds. One of the Russian firms succeeded in getting some thousand barrels direct from the United States, which is selling at prices three times as high as in ordinary times. Gum tragacanth is sold at \$17.11 to \$99.83 per 100 pounds; white dextrin, \$6.42 per 100 pounds. The price of chloride of lime is \$2.85 to \$5.34, but at present the manufacturers are delivering it in limited quantities only, direct to the consumers. Although there is a sufficient supply of pyrites, the works are so busy with Government orders that they produce only small quantities of sulphuric acid for the market, and the supply does not meet the demand. For the same reason there is an insufficient supply of nitric acid, and the price has risen from \$2.85 to \$35.66 per 100 pounds. Castor oil is sold at \$25.67; cocoanut oil from Ceylon at \$29.93; cottonseed oil, \$9.11. Ammonia in powder sells at \$7.14; in crystals, \$15.70; spirits of ammonia, \$4.98 per 100 pounds. There are abundant supplies of potash at the places of production, but there is no possibility of transporting it to Moscow, where a lack is felt. However, the most important soap manufacturers have a sufficient supply of this article to last until June. There is little sulphur in lumps and the prices reach \$14.26 for raw sulphur and \$18.77 for refined. Some works and factories that had purchased a supply of sulphur for their requirements find it more profitable to store their production for the time being and to sell their sulphur at high prices. A steamer with a cargo of about 18,000 tons of Chile saltpeter is said to be on its way to Archangel.

Antimony Shipments From Central China.

According to the Hankow Times, 1,067 tons of antimony regulus and 2,560 tons crude antimony were exported from Hankow during the first three months of 1915. It may be stated that the price of antimony regulus has practically quadrupled since the beginning of the European war. The increased demand has stimulated local firms to put forth every effort to increase the production and with satisfactory results. The following table indicates the quantity and value (in United States currency) of the various forms in which antimony was exported from this port in 1914:

Antimony.	Tons.	Value.
Crude	10,071	\$486,916
Regulus	1,384	88,874
Ore	4,637	100,593
Ore refuse	1,880	7,532
Ore oxide	5,693	75,514
Ore oxide refuse	1,748	9,506
Total	25,413	\$768,935

Antimony appears in Maritime Customs returns as being shipped to Hongkong for final consignment, but probably connections are being formed to enable direct consignments from this port to the purchasers.

New Zinc Factory for Japan.

The zinc industry in Japan is still in its infancy, there being only tow factories—the Amagasaki Zinc Factory and the Mitsui Bussan Kaisha Zinc Refinery. On account of the outbreak of the war the imports of zinc into Japan from Germany and Belgium have been totally suspended. Naturally, the price of the metal, which ruled at \$120 gold per ton before the war, has risen steadily, and now rules at over \$200 per ton. In Siberia there are large zinc mines, the output of which has hitherto been forwarded to Germany and Belgium. With the opening of hostilities the supply of zinc ore to Europe became impossible and prices fell considerably. Taking advantage of this, the Mitsui Bussan Kaisha recently entered into an arrangement with owners of zinc mines for supplies. It is stated that a big zinc factory will be established in Japan in the near future under the auspices of merchants interested, with a view to meeting the demands on the domestic market.

WANTED—Several young graduates in chemistry, chemical engineering and metallurgical engineering for positions with mining, industrial and manufacturing companies; salaries \$60-\$100. The Engineering Agency, Inc. Est. 1893; 23rd successful year. 1662 Monadnock Bldg., Chicago.

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WHAT DISINFECTANT IS THE MOST GENERALLY APPLICABLE FOR CLINICAL, SURGICAL AND SANITARY PURPOSES.*

By HERBERT C. HAMILTON.

Phenol, discovered in 1834, was at first thought to be identical with wood creosote, which at that time was regarded very highly as a disinfectant. This was proved, however, to be incorrect, and, while there were points of resemblance, there were also several properties not common to both. Beechwood creosote is less poisonous and more germicidal than phenol proper, but it is only very slightly soluble, coagulates albumins more completely, and for various other reasons is almost discredited except for a few special purposes.

The discovery by Lister (1871) that suppuration of wounds could in almost every case be prevented by use of carbolic acid gave a great impetus to its use as a germicide and antiseptic. This work was the basis of the whole modern theory and practice relating to micro-organisms, not only as they apply to Lister's special field of surgery but to that of sanitation as well.

Probably no discovery in biology has been more revolutionary and far-reaching than his, since he shares with Pasteur the honor of demonstrating the connection between micro-organisms and processes of infection. Lister found carbolic acid to be exceedingly efficient, and recommended it highly because of its ready adaptability to the processes of aseptic surgery. While it is fatal in three to five per cent solution to the vegetative forms of microbial life, it is not always effective against spores in any dilution or even in pure form except at high temperatures. However, because of retaining its effectiveness in the presence of salts, acids, alkalies, and even protein, it ranks above mercuric chloride for some purposes, although under ideal conditions the latter is many times as efficient.

That portion of coal-tar oil which remains after phenol is removed was first recognized as having antiseptic value when it was used for pickling timber, a process patented in 1836 in England. It is still an open question what constituent of the heavy coal-tar oils is most valuable as a preservative, but its use for this purpose served to direct attention to the strongly germicidal character of certain of its constituents. A part of the oil, later known as creosote oil because of its similarity to wood creosote, was prepared as a disinfectant as early as 1874. The first preparation of importance was that known as creolin, prepared in 1887. It was analyzed, and its composition made known to the scientific world in 1889. Since that time the number of such preparations has increased enormously, and at the present time there are hundreds of the coal-tar disinfectants composed of creosote oil and soap and containing various proportions of phenols. The germicidal values of these range from that with a coefficient of 1, or about equal to pure phenol, to those of exceptional value with coefficients of 10 or more, depending on the amount and character of the phenols present.

The phenol coefficient is a term used to designate the value of a germicide. Since carbolic acid or phenol is well known as an efficient disinfectant, its value is taken as unity, and the value of any other substance similarly used can be expressed by a number called its co-efficient, which indicates how many times more, or in some cases less, the disinfectant can be diluted than phenol and retain an equal germicidal value. Because of the infinite variety of combinations in coal tar, a chemical assay will not give a very accurate indication of the efficiency of an oil. Its real value can be ascertained only by actual comparison with phenol, using *B. typhosus* as the test organism, and finding the dilutions of the sample which are as efficient as certain dilutions of phenol.

These phenols are so called from their resemblance to carbolic acid or phenol proper, and are more or less closely allied to it both in composition and in properties. They differ, however, in several important characteristics. With few exceptions they are liquid and will not crystalline as carbolic acid does; they are very slightly soluble in water, and require a solvent of some character to bring them into a condition in which their activity can be measured and applied; they are much less poisonous and corrosive than phenol, and are more strongly germicidal. Chemically the phenols of ordinary coal tar differ from carbolic acid in having one or more organic radicals attached to the benzol ring. The graphic formula for benzol is theoretically considered to be a hexagon, familiarly known as the benzol ring. Each angle of the hexagon is occupied by a CH group, and on this simple form thousands of organic compounds are built up by additions or substitution.

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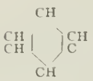
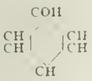
*From Therapeutic Gazette, 1914, p. 311.

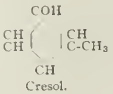
Phenol and cresol or cresylic acid are shown below in their generally accepted formulæ:



Benzol.



Phenol.



Cresol.

It is possible by synthesis to prepare derivatives still more strongly germicidal than those occurring naturally in the coal tar.

The insoluble character of the phenols and of the creosote oil containing them requires the use of an agent to be incorporated with these oils which will allow the formation of a homogeneous solution or emulsion when the product is mixed with water.

Because of the different kinds of oils used and the necessarily different treatments to prepare a substance miscible with or soluble in water, the coal-tar disinfectants differ among themselves. These differences are unimportant except from the view point of efficiency, and on this basis the disinfectants may be classified into three groups:

Group 1, those with a phenol coefficient of about 2 which are soluble in soft water, to make a clear solution. Compound Solution of Cresols U. S. P. is an example of this group.

Group 2, the ordinary type of coal-tar disinfectants with coefficient of 2 to 6 which emulsify when mixed with warm, soft water.

Group 3, the high coefficient disinfectants which also emulsify when mixed with water, but which are efficient when much more highly diluted.

There are certain advantages in using these coal-tar derivatives which make them far superior to most other disinfectants. These may be summarized as follows:

Convenience.—Compared with dissolving carbolic acid crystals to make a three to five per cent solution it is much easier to dissolve any member of these groups. Some can be dissolved in water in any proportion; any one, if properly made, can be dissolved readily to make a stronger solution than is possible to obtain with carbolic acid crystals.

Efficiency.—The members of Group 1 will dissolve readily to make a solution of any desired strength, from that of pure carbolic acid down to one that is merely antiseptic.

The members of Group 2 are more efficient—a one or two per cent solution usually far exceeding the efficiency of the strongest solution of phenol.

The members of Group 3 are still more efficient, as their phenol coefficients indicate.

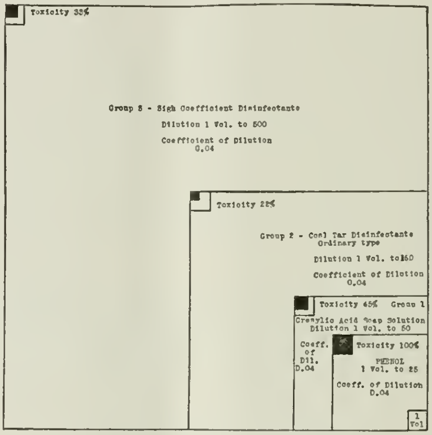
Safety.—The coal-tar disinfectants are practically neither toxic nor corrosive when diluted for use on the basis of their efficiencies.

Character of Solution.—The formula for almost all the coal-tar disinfectants is such that the solution is alkaline and soapy, which aids its penetration. There is very little if any coagulation of protein to hinder penetration and lower the efficiency.

It is evident from the above comparisons that the proper use of the coal-tar disinfectants represents a distinct advance over that of carbolic acid. Even the one factor of safety alone is sufficient reason to exclude the latter from general use.

Comparing the coal-tar disinfectants with those of the metallic salts and gaseous disinfectants, the most important point to be considered is:

Adaptability.—Sulphites and sulphurous acid and ferrous salts are strictly limited in their usefulness to such conditions where the abstraction of oxygen or water is detrimental or destructive to the life and development of bacteria, etc. Calcium hypochlorite and potassium permanganate are valuable where bacterial life is endangered by the action of oxygen, these substances being oxidizing agents either directly or indirectly. It is evident, therefore, that such substances are not generally applicable as disinfectants. For purifying water or sewage where oxidation of organic matter is as important as germicidal action the oxidizing agents are especially adapted.



Group Classification of Disinfectants.

Mercuric chloride, while being highly efficient under exceptional conditions, is so readily destroyed or so lowered in efficiency under ordinary conditions that it is not a dependable disinfectant. It is precipitated by protein, soap, and sulphur compounds; it is limited in its penetrating properties because of the coagulating action on albumin; it inhibits the growth and does not kill organisms after short exposures; it is exceedingly poisonous and irritating.

Formaldehyde is limited in its usefulness to its application as a gaseous disinfectant. In this field no preparation can replace it; but a solution of the gas in water applied as a liquid disinfectant is far inferior to phenol.

The comparisons made above indicate that even the ordinary coal-tar disinfectants when properly prepared are superior to phenol under all conditions, and surpass all other disinfectants aside from the purposes for which the latter are peculiarly adapted.

Recently coal-tar disinfectants of much higher efficiency have been prepared. The coefficients of some of these in fact are so high that the correctness of such statements is seriously questioned. The origin and chemical character of the oils from which these are prepared are more or less indefinite. Whether the character of the coal or the method of distillation by which the oils are produced is responsible for the high germicidal value is not generally known. That it is not produced in America might indicate that the character of the coal is at least partly responsible for the difference. The methods used in producing gases from coal for use in the steel and iron industries differ in England from those followed in America. It is a well-known fact that the temperature maintained and the presence or absence of air, during the destructive distillation, very markedly influence the character of the resulting products. In one case the benzols appear to oxidize to phenols, in another they appear to polymerize to naphthaline, anthracene, etc. This being true, it may be that still another series of compounds results from a slight difference in the conditions obtaining during this destructive process. The chemical composition has been claimed by Worrall (Rideal's "Disinfection and Disinfectants") to be such as to place them among the organic compounds that are entirely different from the phenols of coal tar. Another writer attempts to throw a veil of mystery over them by assigning them to the class of diphenyls.

For the purpose of this article the composition and structure of those high coefficient oils are unimportant. The sanitarian is more concerned with the efficiency of the disinfectant prepared from them. Is there real value in it in proportion to the claimed efficiency? Can confidence be placed in the statement of its value when this so far exceeds that of phenol and similar disinfectants? The question may also suggest itself. How is it possible that a product less toxic and less corrosive than carbolic acid, practically harmless when diluted as it can and should be before using, is so exceptionally active that bacteria are killed in dilutions fifteen to twenty times as great as can be safely recommended for phenol?

The average user of disinfectant rarely knows from results whether it is efficient or not, because he has neither the facilities nor the skill to test it, and because incomplete disinfection or entire absence of it may not be followed by any infection directly traceable to such a failure. Even the chemist, however familiar he may be with disinfectant oils, cannot determine with certainty the efficiency of any product entirely by its chemical properties. Bacteriological rather than chemical control is, therefore, a very essential requirement for disinfectants. Hygienic measures are too vitally important to be open to suspicion regarding the substances used. The methods of applying them are so often open to question that the substances must be in the highest degree efficient.

The ideal disinfectant has been described in great detail by different authors. But the ideal disinfectant for every kind of disinfection is probably unattainable and its desirability questionable.

Formaldehyde, mercuric chloride, silver nitrate, phenol, and the coal-tar derivatives each has its sphere of usefulness, and each is more or less ideal in that sphere. Where a coal-tar derivative is applicable, however, there are certain properties possessed by this class of high coefficient disinfectants which very closly approach the ideal for general disinfection.

The average coal-tar disinfection of Group 2 is used in a solution of one per cent, in which dilution it is about as efficient as a three to five per cent solution of phenol. One of the disinfectants of Group 3, with a phenol coefficient of 20 when diluted to a one per cent solution, is four times as efficient as a five per cent solution of carbolic acid crystals. The accompanying chart is a grapic representation of the comparative efficiencies and toxicities of representatives of the three groups. The "1 Vol." square is shown in the lower right-hand corner, while the four largest squares show the volumes to which this one volume of phenol and of each of the three groups can be diluted, all of the dilutions having the same germicidal efficiency—a phenol coefficient of 0.04.

The toxicities are shown graphically by the square in the upper left-hand corners of the four squares representing the dilutions. Phenol, being used as a standard, is entirely black, while the others are blackened in proportion to their toxicities, expressed in per cent of that of phenol. The ratio of the black "toxicity" squares is a graphic representation of the non-toxic character of these dilutions compared to that of phenol. For example, Group 3 with a toxicity of thirty-three per cent has a black square one-third as large as that for phenol; a comparison of the two toxicities with their corresponding dilutions shows that a solution of phenol is sixty times as toxic as a member of Group 3 diluted to an equal efficiency.

The coagulative action and the caustic and corrosive properties of the three groups can be only roughly measured; these seem, however, to be very closely associated with toxicity. So the practically harmless nature of Groups 2 and 3—particularly the latter—is evident from the chart.

Instruments are not corroded, nor is there any irritation to the healthy skin, when immersed in such a solution. The mucous membrane, however, being more sensitive will tingle and smart from application of this solution because of its alkaline and penetrating character.

Coal-tar disinfectants in general are, like phenol, unaffected by alkalies. While their values are diminished by organic matter more than is phenol, this is apparently a slower action rather than actual lowered efficiency, since there is almost no coagulation of the organic matter. In this case the fact that the disinfectant is in emulsified form explains its slow action, because necessarily the minute globules of oil composing the emulsion require a more prolonged period to penetrate moist organic matter, which tends to retard penetration.

Acids do not destroy but do materially impair the value of emulsified disinfectants in which the vehicle is soap. The same is true of hard or salty water. It is easier, however, to correct these waters or replace them with soft water with which to dilute a disinfectant than to replace soap by any other emulsifier of equal efficiency. Soap has several valuable properties in addition to that of being an efficient emulsifier of coal-tar oils. It is cleansing and tends to dissolve the natural, protective, greasy coating on the skin and other surfaces. It is not devoid of germicidal action in itself.

As a deodorant a coal-tar disinfectant has an action tending to absorb, remove, and replace bad odors. Its real value, however, is to destroy the putrefactive bacteria producing the odors—the only property which makes a deodorant of real value.

An emulsified disinfectant has been proved to exceed a soluble disinfectant even if the same constituents and the same proportion were present in each. This is shown to be due to a concentration of the minute globules of oily emulsion around the bacteria, the results being equivalent to those from a considerably stronger solution in which no minute globules of oil are present, but all is in uniform solution.

To summarize, a high coefficient disinfectant of the third group is less likely to be destroyed or inhibited in its action and is more generally applicable than the gaseous disinfectants, the oxidizing and reducing agents, or the toxic and protein-coagulating agents.

When diluted to make a solution equivalent to a three or five per cent solution of phenol, it is

Non-toxic.
Non-corrosive to metals.
Non-coagulative to tissues.
Not caustic to the skin.
Not affected by alkalies.
Not destroyed by acids.
Not oxidized nor reduced by organic matter.
An efficient germicide.
At minimum cost per unit of efficiency.

It is not merely a substitute for carbolic acid; it is a new material possessing not only all the advantages of this valuable substance, but many others in addition. Why should the physician or the surgeon continue to use carbolic acid?

POTASH FROM KELP.*

By THOMAS H. NORTON.†

The Bureau of Soils in the Department of Agriculture has issued a most timely and important monograph on the kelp beds in the Pacific found off a large proportion of our littoral, including Alaska.

The report in question bears the title "Potash from Kelp," and is prepared by Dr. Frank K. Cameron, who has the supervision of chemiscal, physical, and fertilizer investigations. It presents in compact form the results of an enormous amount of marine exploration and analytical work in the laboratory. Nothing has been omitted which is requisite for an adequate knowledge of the extent of the beds, the local characteristics, the percentage of potash and other valuable constituents present, the facilities for exploitation, and all the other factors which may eventually come into play, in any attempt to utilize on a generous scale, the great possibilities of this magnificent national asset.

The report in question is based upon the results obtained in 1912 and 1913 by four well-equipped survey parties cruising in sailing craft or motorboats. One party investigated the entire sea coast of Washington, Oregon, and California, extending its researches along Lower California. Another was occupied with the beds in Puget Sound. A third devoted itself to the archipelago off southeastern Alaska. The fourth party studied the waters about Kokiak Island, Kenai Peninsula, and western Alaska generally.

In all cases the beds have been carefully charted and the relative values of the different stands estimated. The total tonnage of annual crops for each locality has been closely approximated, and the conditions under which harvesting can be pursued have been noted.

NATURE OF KELP.

The general results of this noteworthy survey may be summarized as follows:

Among the many varieties of algæ (sea-weeds and rockweeds) growing along the Pacific coast three are of pronounced commercial importance, containing large amounts of potash and occurring in vast quantities. These are Macrocystis pyrifera (California kelp), Nereocystis luetkeana (bull kelp or bladder kelp), and Alaria fistulosa (string kelp). Some other varieties contain higher percentages of potash, but occur only in scattered groups or are not available for other technical reasons.

The three varieties differ widely in appearance and in peculiar characteristics, as evidenced by the nature of the surroundings in which they flourish best, depth of water, resistance to breakers or ocean swells, attractiveness to certain animal enemies, etc. In general they all have a holdfast, a group of tentacle-like branches not unlike the roots of land plants, by which they are anchored to rocks or some other relatively immovable substance. The stem rises from the holdfast to the surface, terminating in the "float," a hollow organ of thick, fleshy walls, filled with air, and in consequence remaining on the surface of the sea. The fronds or leaves extend from the float. The tissues of kelp contain little or no fiber. They are easily crushed to a pulpy mass, and in this condition pass through ordinary filtering materials.

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*From The American Fertilizer.

†Commercial Agent United States Bureau of Foreign and Domestic Commerce.

Stems of Macrocystis average 100 feet in length, but lengths of 1,000 feet are encountered. The leaves are usually 14 inches long. Alaria has very short stems, but the leaves average 40 feet in length. Both of these varieties are perennials. Nereocystis is an annual.

VALUE OF KELP.

The amounts of soluble salts and nitrogen compounds present in the various beds of the same kind of kelp vary very largely. Thus in different samples of Macrocystis potash varies from 3.1 to 27.7 per cent; nitrogen from 0.53 to 3.17 per cent. The averages of a great many analyses are as follows:

Macrocystis—K_2O, 12.59 per cent; N, 1.57 per cent; iodine, 0.23 per cent.

Nereocystis—K_2O, 20.1 per cent; N, 1.9 per cent; iodine, 0.13 per cent.

Alaria—K_2O, 9.1 per cent; N, 2.6 per cent; iodine, trace.

Dried kelp contains ordinarily about 15 per cent of potash, 2 per cent of nitrogen, and 1.5 per cent of phosphoric acid (P_2O_5). It serves admirably as a manure alone, and can be used most advantageously in the manufacture of special and complete fertilizers. The harvesting of kelp, as practiced thus far, by "mowing" the beds at depths of 12 feet or less (usually 4 to 6 feet), is followed by a rapid reproduction of the plants in the case of the perennials, very much as is the rule with clover or alfalfa. Along the southern section of the coast two cuttings annually are quite practicable without affecting the permanent value of a bed. Nereocystis is not harvested until the spores are well ripened. Otherwise enough plants must be left in each bed to insure reseeding.

DISTRIBUTION OF KELP.

The results of the present survey show that the commercially available kelp beds of the Pacific Coast and the annual harvest of kelp, with its resultant equivalent of potassium chloride, are as follows:

AREA AND TONNAGE OF PACIFIC KELP BEDS.

Region.	Area, sq. miles.	Fresh kelp, tons.	Potassium chloride, tons.
Cedros Island to San Diego......	91.4	16,979,800	649,000
San Diego to Point Conception...	97.9	18,195,300	696,000
Point Conception to Cape Flattery	36.2	4,377,400	167,000
Puget Sound....................	5.0	520,000	20,000
Southeast Alaska...............	141.6	15,666,000	598,000
Western Alaska.................	17.9	3,367,000	136,000
Total	390.0	59,305,500	3,206,000

It is evident from the above that southeastern Alaska and the southern California coast offer the best fields, as does also the extensive stretch along the Mexican coast of Lower California to Cedros Island. The annual tonnage for this section, as well as for the adjacent section, from San Diego to Point Conception, is based upon two cuttings each season.

POTASH SALTS AVAILABLE.

The above figures show that the shallow waters of the Pacific coast, within the jurisdiction of the United States, are producing each year, without cultivation, a crop which, if simply collected and dried, possesses, as a fertilizer, at the customary ante bellum prices for potash and nitrogen, a value of over $150,000,000.

If used as a source of commercial potassium chloride, the final product would have a value of $90,000,000.

ECONOMIC IMPORTANCE.

It would appear to be thoroughly feasible to so organize the harvesting and drying of kelp along the Pacific littoral that our fertilizer industry can be promptly emancipated from dependence upon the potash salts of Germany.

The data supplied in Dr. Cameron's report are of far-reaching importance, as furnishing a trustworthy basis for the establishment upon American soil of domestic production of the salts in question, and the subject deserves full consideration in view of the urgent need at present for potash compounds by agriculture, manufacturers of explosives, glass makers, and nearly every phase of chemical industry.

IMPORTS OF POTASH SALTS FOR USE AS FERTILIZERS.

During the fiscal year 1913-14 the importations into the United States of potash salts from Germany, for use as fertilizers, amounted to 1,060,000 long tons. This total included 238,000 tons muriate of potash (containing about 80 per cent KCl), 45,000 tons of sulphate (90 per cent), 261,000 tons manure salts (averaging 20 per cent K_2O), and 526,000 tons kainit (averaging 12.4 per cent K_2O).

This entire amount was equivalent to 413,000 tons of pure potassium chloride. It represents approximately the current annual needs of the American fertilizer industry, as far as potash is concerned. Referring to the estimated product of our Pacific coast as tabulated above, it constitutes but one-eighth of the annual output theoretically available.

The important problem before American chemical industry is how to transform a sufficient portion of this floating mass of kelp into a dry product and transport it to our Gulf ports and Atlantic ports at a combined cost materially below what has normally been paid in the past for cargoes of German potash salts laid down at these points, where the fertilizer industry is chiefly centered.

PRICES OF GERMAN POTASH SALTS.

The prices for the German salts delivered at Gulf and Atlantic ports before the outbreak of the present war were as follows:

	Per cent K_2O	Price (Short Tons)
Muriate of potash, 80 per cent KCl	50	$38.05
Sulphate of potash, 90 per cent K_2SO_4	48	46.30
Manure salts	20	13.30
Kainit	12.4	8.25

A discount of 15 per cent from these prices is granted to purchasers of large quantities in bulk c. i. f.

The ocean-freight rates on these salts, in bulk, from Hamburg averaged $2.07 per long ton.

It is probable that transportation rates by water via the Panama Canal from San Diego and vicinity would not vary much from the Hamburg maritime rate.

Assuming a freight rate from the Pacific coast to the Atlantic coast of $2 per short ton, and deducting 15 per cent for prices in bulk, the cost of production of dried kelp, f. o. b. California ports, should be such that it can compete easily with the German salts at the following net rates per short ton:

Muriate of potash, 80 per cent	$30.50
Sulphate of potash, 90 per cent	37.40
Manure salts	9.60
Kainit	5.30

COST OF COLLECTING.

The production of dried kelp as a commercial article involves two distinct items of cost, (1) the gathering of fresh or wet kelp, and (2) its desiccation, with the incidental charges of storage, handling, grinding, and loading on ocean vessels.

1. The operation of cutting and collecting fresh kelp has now been well systematized and organized. As conducted at present, after the experience of two or three years, it does not exceed 20 cents per ton. (A description of the operation is found in Commerce Reports, No. 137, for June 12, 1915).

The amount of dried kelp obtainable from wet kelp varies according to the plant. From 100 tons of fresh Macrocystis the average yield is 13.2 tons, containing 2.53 tons K_2O; from Nereocystis, 8.6 tons containing 1.6 tons K_2O; from Alaria, 13.7 tons, containing 1.33 tons K_2O.

Leaving out of question for the time being the Alaria found only along the Alaska coast, and considering only the other two varieties, it is found that on an average 100 tons of wet kelp yield 10.9 tons of dried kelp containing 18.9 per cent K_2O, 2 per cent N, and 1.5 per cent K_2O_5. On this basis the operation of cutting and collecting the material for 1 ton of dried kelp costs $1.83.

COST OF DRYING KELP.

2. The cost of drying kelp has not yet been made a subject of careful study. On the Mexican coast of South California, rapid air drying is feasible. Proceeding northward along the coast, climatic conditions become less and less favorable, an artificial drying seems unavoidable. According to the locality, kelp might be more or less dried by exposure to the open air for a short time. The operation could be completed by using a rotating drum or tube, types of which are common in various branches of manufacture. The kelp entering at one end of a tube, issues dry at the other end, and falls upon a conveyor. A current of heated air passes through the tube in the opposite direction and takes up the moisture. Conditions require the removal of nearly 8.2 pounds of water for each pound of dry kelp produced. Laboratory observation shows that kelp is more readily dried in such devices than tankage, garbage, and fish scrap, all of which are efficiently and economically desiccated in drums or tubes.

It would appear doubtful whether the cost of handling, drying, grinding, storage, and loading, at San Diego and vicinity, would much exceed $1 per ton of dried kelp, when the industry is organized upon an extensive scale.

VALUE OF NITROGEN AND PHOSPHORIC ACID PRESENT.

In considering the value of dried kelp for a fertilizer, especially in connection with transportation problems, the amounts of available nitrogen and phosphoric acid present are important factors.

On the basis of 2 per cent of nitrogen and 1.5 per cent of phosphoric acid, a short ton of dried kelp contains the equivalent of 258 pounds of Chile saltpeter, valued at current rates at $5.93, and of 192 pounds of superphosphate (15.5 per cent), value $0.75. The total fertilizer value of a short ton of dried kelp, entirely apart from the potash present, is therefore $6.68.

VALUE OF POTASH PRESENT.

In point of potash content, the dried kelp approaches very closely the category of imported German potash salts, termed manure salts, with a minimum of 20 per cent K_2O. On the basis of the rate in the table given above, viz., $9.60, the potash in a short ton of dry California kelp is worth $9.07.

The total value based upon potash, nitrogen, and phosphoric acid is $15.75.

COST OF PRODUCTION—MARGIN OF PROFIT.

Against this market value is to be placed the cost of production per short ton, as outlined above:

Cutting and collecting	$1.83
Drying, grinding, handling, loading, etc. (estimated)	1.00
General expenses, interest, etc. (estimated)	1.00
Total	$3.83

The margin here of nearly $12 is such that all closely identified with the interest of the fertilizer trade should study the possibilities of promptly utilizing the vast resources of our Pacific littoral. We have been expending annually for low-grade kainit and manure salts $5,330,000. The equivalent supply can be furnished by our own kelp beds, without having recourse to other operations than those of a purely mechanical nature.

In the case of the more concentrated muriate and sulphate of potash, which we import annually to the value of over $9,800,000, the margin of economy would be somewhat lessened, but not materially. It must not be forgotten that dried kelp, after deduction of the normal nitrate and acid phosphate present, carries 24.4 per cent of K_2O, and is to be regarded as such, when used for making complete fertilizers. Unquestionably, with a slight chance of formulas and standards, the major portion of the muriate and sulphate now imported from Germany for fertilizer purposes could be effectively replaced by the American product with pronounced economy on the basis of antebellum prices.

Needless to say, with muriate now selling at $205 per ton instead of $38, there is every inducement for the quick utilization of the Pacific beds.

OTHER POTASH COMPOUNDS.

We import other potash compounds to the value of $1,700,000 annually, including the carbonate (92,000 tons) and saltpeter (1,580 tons). The technical process for the economical separation from kelp of potassium chloride in a more or less pure form may require time for development, but we can count confidently upon an early solution of the problem and the ultimate emancipation of American industrial chemistry from dependence upon a single, distant, foreign source of potash.

SIMILARITY BETWEEN THE POTASH AND DYESTUFF SITUATIONS.

There is a striking similarity between the dyestuff situation and the potash situation in the United States. In both cases the country possesses the raw material in the greatest abundance, and the consumption of final products is enormous. Yet for both categories of compounds the United States depends upon German sources. The potash famine and the dyestuff famine, affecting so seriously the interests of American agriculture, of the great textile industries, and of sources of allied branches, should work like a leaven to stimulate capital and enterprise to bring about a prompt and permanent change in the existing dependence upon foreign effort and intelligence.

JURISDICTION OVER KELP BEDS.

The kelp beds along the Pacific coast are, with insignificant exceptions, inside the 3-mile limit at mean low water, and are subject to the jurisdiction of the several States within whose bounds they lie, or of the Federal Government in the case of Alaska. The paramount right of the Federal Government to regulate commerce and navigation naturally extends to the areas in question.

At present the collection of kelp is free to all. Statutory regulation will inevitably be necessary at an early date in order to give capital the needed assurance of security in making large investments, and to insure the permanent conservation of the great beds.

KELP CULTIVATION.

For the immediate future the potash question evidently demands nothing beyond a rapid and intelligent utilization of the immense supply of kelp as nature has provided it, due regard being paid to the conditions requisite for uninterrupted annual reproduction.

Dr. Cameron's monograph cites, however, the occurrence, in small quantities, of varieties of kelp which contain notably higher percentages of potash than is the case with the three varieties mentioned above, found in such abundance and constituting at present the only supply of industrial importance. For instance, the variety Pelagophycus porra, or elk kelp, has uniformly a higher content of potash than any other known kelp. It is found throughout the area of kelp beds off the coast of Lower California, but only in scattered groups and single plants along the seaward edge of the great Macrocystis stands.

There would appear to be here a distinct opportunity for investigation under Federal auspices as to the possibility of eventually substituting beds of Pelagophycus for the existing stands of other varieties. This would involve an intimate study of the life history of the varieties concerned. Apparently the best promise of success would be offered by the fields of Nereocystis, which seems to depend so largely on annual propagation from the spores formed on the leaves.

As the percentage of potash in Macrocystis is, however, so conspicuously inferior to that of Nereocystis, and the former predominates in the localities apparently favorable for the isolated growths of Pelagophycus, any study leading to the successful substitution of the last mentioned for the chief variety found in the San Diego region would be of prime importance.

Each added per cent of potash in the final product of dried kelp diminishes by so much the cost of production and the transportation charges per effective unit of alkali, and increases the value of the kelp as raw material for the manufacture of technical and pure potassium compounds.

Satisfactory proof that the productive power of the areas, now distinctly favorable to the growth of the most valuable variety of kelp, are economically susceptible of a pronounced increase, would be a powerful factor in attracting capital to this field.

This report of the Bureau of Soils supplies in a most comprehensive form all of the physical, physiological, and topographical data needed by those interested in building up a national industry. It is accompanied by 40 fine plates, illustrative of the occurrence, appearance, life history, and collection of the three important varieties, and by a portfolio of 54 large maps, showing in detail the location, density, and character of the kelp beds of the Pacific coast, including Alaska and a part of Lower California.

The report, with its portfolio of maps, can be secured by application to the Superintendent of Documents, Government Printing Office, Washington, price $2.

Arrangements are being made for the erection of a large factory in Sweden where peat powder will be prepared. It will be located in the Province of Vastergotland, where there are many large peat bogs.

FRACTIONAL COLLECTION OF CRUDE TAR.*

By G. T. PURVES.

The collection of crude tar in fractions does not appear to have received the attention its importance justifies. Apart from the purely commercial aspect, it is worth considering how far the primary separation of crude tar into the usual first fractions in the closed condensing system would be helpful to the reduction of atmospheric pollution. In some tar works the gases evolved from the tar are burnt direct, and in others passed through purifiers. In the case of direct fractionation, this gas would go to augment the volume of permanent gas produced.

If tar can be collected in the ordinary practice of carbonizing in those fractions into which the distiller ultimately splits it up, this would clearly be a desirable attainment, provided the cost of so doing is not excessive.

It is known that in the distillation of tar decomposition of certain products occur, and the content of free carbon is increased. I have distilled a sample of heavy crude tar, liquid at ordinary temperature, and after remixing the fractions, warming and allowing to cool, the product was solid, showing considerable alteration in the component products. Such a change might in some cases be beneficial, but in others would be objectionable. Direct fractional collection avoids the submission of the heavy tar to the high temperatures obtaining in the still towards the end of the distillation. The object in this paper, however, is to consider the question from the carbonizer's rather than the tar distiller's point of view.

In gas-works practice the crude gas from the retorts is commonly drawn through a liquor seal in the hydraulic main, and here heavy pitchy tar is deposited. Later in the slow condensing main, then in the final coolers and tar extractors, and lastly in the distribution system, lighter and lighter fractions are separated, in each case by cooling and frictional scrubbing. This is distinctly fractional separation of tar, but the carbonizer carefully runs his fractions into the common tar well.

It will be interesting to consider one or two factors that have governed practice in tar extraction and their effects on the gas, on by-product recovery, and also on the trend of development towards complete direct fractionation. Before doing so, however, I wish to refer to the nature and removal of tar fog. When the fog is first precipitated in the gas, it must be in an extremely fine state of division, and the question arises, How fine? In a recent descriptive paper on the "Electrical Separation of Tar from Gas," the following statement is made referring to the paper-stain method of determining the amount of tar in crude gas: "When the gas carries large quantities of tar mist the aspirator bottle will be full of the dense brown fog which has passed through the papers"—*i. e.*, two filter-papers. In the face of this, no practical tar-scrubber could be expected to remove such fog completely. At the actual moment of condensation, the minute drops of a liquid would all be of the same size, and consist of the smallest number of molecules that could satisfy the conditions of equilibrium for the liquid state.

In order to remove tar fog it is necessary to allow sufficient time to elapse for the elementary liquid drops to agglomerate to the relatively large drops that we are able to deal with in practice. The size of the globules will be increased not only by aggregation, but also by the solution in them of other vapors from the gas. I find a recognition of this principle in the process of Henry Aitken, patented in 1874: "the settling of tar fog was promoted by sending gas at 190° Fahr. into a very large settling chamber and keeping it there for as long as possible at that temperature." The point I wish to make is that tar fog cannot be simultaneously precipitated in the gas and removed by frictional means from it.

When the candle power of gas was higher than it is today, slow cooling of the gas was favored as a means of keeping up candle power by retaining in the gas as vapor a larger amount of the illuminating condensable hydrocarbons. In the Saxon industry, where lignite is carbonized for its tar products, we find "the cooling effect is produced solely by external air; and it is important that the vapors should pass through as long a track of tubing as possible. It has been found that if the vapors are cooled by water in a short condenser to the same temperature as in the atmospheric condenser, they will contain condensable constituents, whereas these are almost entirely absent when air is used. The most important point in the condensing process is the gradual cooling." Exactly opposite results are thus apparently claimed for the same operation.

As the crude gas from the retorts cools down, its dew points with respect to different hydrocarbons, etc., are reached one after another, and the substances settle out as constituents of tar fog. The minute drops comprising the fog float in the gas for a considerable time, depending largely on their specific gravity and the frictional resistance encountered. The tar fog has a solvent action on those hydrocarbons, etc., still present in the gas as vapors, provided the temperature is not above their boiling points; and it will dissolve a proportion even when the gas has been cooled down to its dew point with respect to the particular substance. If the fog remained in the gas for a sufficient time, a state of equilibrium as regards solution would be established when the vapor pressure of the substance in the fog equalled the partial pressure of the substance in the gas. Hence by passing the gas through a slow condensing main where the fog globules will coalesce and settle out of the gas slowly, the gas is largely denuded of its light oil constituents, as is claimed in the lignite industry. Lignite carbonizing being a low temperature process, a considerable proportion of the tar produced is very light specifically, and so the fog settles from the gas.

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*From the American Gas Light Journal; abstract of a paper read before the Scottish Section of the Society of Chemical Industry.

The explanation of how the slow condensing main of the gas works helps to keep the lighter hydrocarbons in the gas is to be found partly in the nature of the tar produced, but largely in the higher outlet temperatures at which the slow condensing main is operated. By fractionally collecting the tar, I found in a particular test that the gas produced was capable of carrying as vapor at atmospheric temperature and pressure all the light oil produced. The cooled gas contained 3.5% of hydrocarbons absorbable by fuming sulphuric acid. All the tar present as fog at 80° C. was scrubbed out, and amounted to about 2.75% of the weight of coal carbonized, and contained only a trace of solvent naphtha. By further quick cooling and scrubbing in cold water sprays to about 20° C., some 0.13% of crude naphthalene crystals is obtained. So that by the time the gas has cooled to 80° C., about 95.5% of the tar that has to be removed by the extractors has separated out as fog. If now such a crude gas at 80° C. were passed through a slow condensing main, the fog would be steadily removed while the gas cooled relatively very little; and so the tar fog would have a much reduced opportunity of exerting any solvent action on the hydrocarbon vapors in the gas, with the result that these would be largely retained by the gas, and the candle power enhanced. As the temperature at which the slow condensing main is operated is lowered increasing amounts of benzene vapor, etc., would be removed from the gas. It is probable, however, that at temperatures even much lower than 80° C. little benzene would be removed, for the gas is considerably below the saturation point with regard to this vapor.

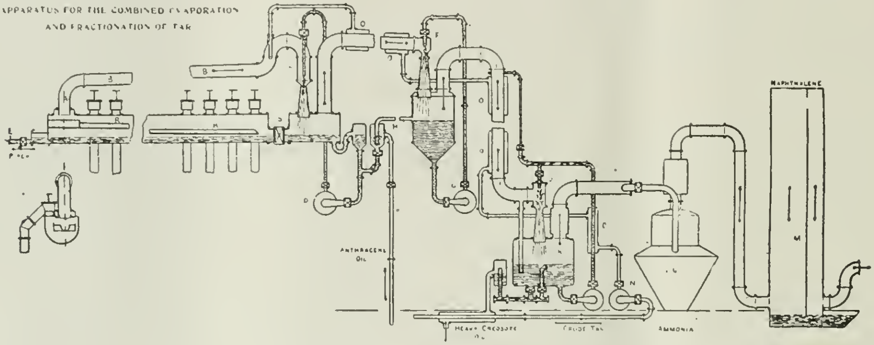
The principle involved is clearly the retarded cooling of the gas while the bulk of the tar fog is removed. The time occupied in the operation does not appear to be a material factor. The ideal state would be the complete removal of all tar fog before the gas reached the temperature at which the light hydrocarbons would be dissolved. This is fractional tar collection in a degree. Professor Lewis writes: "It was realized that sudden cooling of the gas and condensation at too early a period affected the illuminating power more than slow cooling. This is partly due to the tar being thrown out as a whole, while with slow cooling some of the benzene is carried away as vapor by the gas, etc." It is not, however, speed of cooling, but rather one of time contact between tar fog and cooled gas, that is the material factor. For, as has been shown above, the crude gas can be quickly cooled, and the condensable tar removed almost wholly in one and completely in two operations, with practically no removal of benzene. At the Grant gas works, the slow condensing main is upon the counter current principle, and the condensed tar has the minimum opportunity for solvent action on the gas. The slow condensing main at the Greenock gas works is on the direct current principle, and the condensed tar has here the maximum opportunity for solvent action on the gas.

The important point in the working of the slow condensing main is that the outlet temperature shall not be low enough to permit of the benzene, etc., being absorbed. Dr. H. G. Colman, when working on the removal of the heavy tar fog from the hot gas (about the year 1897) had two special objects in view—first, to remove the naphthalene more completely from the gas in the condensers, and, secondly, to retain more of the vapors of the light oils in the gas, and thereby increase the illuminating power. To effect these results he proposed to pass the hot gas through a "Cyclone" extractor. The gyratory motion imparted to the gas in such an apparatus causes a centrifugal action greater in the tar drops than in the surrounding gas, and the tar is thrown to the periphery of the separator, where they coalesce and can be drained away. With the ratio of naphthalene to light oils obtaining in those days, these objects were achieved. But with the larger production of naphthalene in later carbonizing practices, it was found that the crude naphthalene, etc., came down in a semi-solid mass in the condensers and blocked them. In Dr. Colman's method, partial tar fractionation was thus used as a means of overcoming two definite carbonizing troubles.

As we would expect, the writings of William Young are rich in reference to fractional condensation of tar. In the Young and Aitken process, the central feature was the analyzer, in which fractional condensation was carried out. No effort was made, however, to collect separately the tar fractions deposited in the different sections of the analyzer. The tar was allowed to flow downwards from section to section, so allowing the gas to take up as much of the lighter constituents of the tar as possible—this being the principal intention of the process. Fractional condensation with a counter current flow of condensed products thus took the place of sending the gas and condensed products in the same direction. In an address in 1876 on "Condensation," Young showed that, to retain the highest lighting value in the gas, we must keep the gas and condensed tar warm until they have physically separated; and in order that the tar particles may settle out the crude gas must be kept warm and be allowed to travel slowly, and, further, that the tar be allowed to cease contact with the gas only at such a temperature that it could not absorb the lighter hydrocarbons. In other words, there must be the shortest time contact between condensed tar and cooled gas. In later years, when the ratio of naphthalene to light oils in the gas has largely increased, he abandoned the principal of the Aitken and Young process on account of the fact that when it was applied the cooled gas was saturated with naphthalene vapor. With possibly the exception of the gas produced in continuous vertical retorts, complete tar fractionation will always leave the gas saturated with naphthalene vapor when a high carbonizing temperature is applied.

The failure of Brunck's direct ammonia recovery process was principally due to deposits of tar in the saturator, resulting in highly discolored and unmarketable sulphate. This difficulty was overcome in the Koppers semi-direct process by cooling down the gas, then removing the tar, and after reheating the gas passing it through the saturator. Reverting to the original idea of Brunck, Dr. Hilgenstock, of the Otto Company, perfected his process of scrubbing the crude gas with a spray of hot tar, completely removing the tar fog without cooling the gas below its dew point temperature with regard to water, then passing it through the saturator. After passing the saturator, naphthalene and light oils are removed by cooling and scrubbing with creosote oil. In the Simon-Carvés direct recovery process, before the gas reaches the saturator tar is removed in two separate fractions, based principally upon their different specific gravities, but partly on different temperatures. The first is removed in a "Cyclone," and the second in a patent "dynamic extractor," where a more intense centrifugal action is used, and the remaining tar fog completely removed. We thus see that the success of the direct ammonia recovery process is dependent on the fractional separation of the tar.

In 1907 Walter Feld proposed to scrub the crude gas in his patent washer successively at 160°, 80°, and 60° C., and so obtain (as separate fractions) pitch, a heavy oil, and a lighter oil. He further developed his process to include the extraction from the gas of naphthalene, ammonia, and cyanide, etc. To get the pitch fraction, the gas from the collecting main is passed through heat-insulated pipes into the first washer at a temperature from 200° to 160° C.; the latter temperature given by Feld as the dew-point temperature of the high-boiling-point hydrocarbons constituting the pitch. The washing oil in the upper part of the washer is a solution of pitch in a portion of the next condensate, and in the bottom chambers the pitch fraction itself. Before the gas enters this washer it must have deposited an almost solid pitch containing a large proportion of the free carbon. It is difficult to see how this can be worked up with the true pitch fraction on the lines of the Feld process. This appears to be borne out to some extent by the fact that soft pitch produced by the process contains only from 1% to 3% of fixed carbon, less than is usually found in crude tar. If the crude gas enters the first washer at the high temperature, and the fall of 40° C. takes place there, it is fairly certain that some of the fog then produced would pass this washer, and so lower the efficiency of the fractionation. This difficulty would be experienced in each washer where a fall of temperature occurred. Such a procedure is, in fact, attempting simultaneous production and removal of fog. Feld seems to have expected, or else found, this difficulty, for he proposed to improve the fractionation and to lower the temperature of the gas at one stage by pumping into it a portion of the product extracted at a later stage. This, on evaporating, would leave behind some of the former fraction which had been carried forward. In this way he no doubt partially helps the fractionation.



Sketch of Apparatus for Tar Evaporation and Fractionation.

Two years ago Dr. Davidson expressed the view that the partial fractionation of the tar by the sensible heat of the crude gas could be simply effected on vertical retort and coke-oven installations; and described a method of producing in the gas-collecting main, in addition to the crude tar, a distinct and marketable pitch fraction which would certainly be lower in free carbon than that obtained in ordinary practice. Briefly, his method is as follows: In the collecting main of the Dessau retorts an agitator works continuously. A few minutes before the draw, tar is run into the main to a depth of 10½ inches, and when the charging of the nine retorts is complete the level of the tar in the main is brought down to 4 inches. During the ensuing carbonizing period, the remaining tar, due to addition of pitch from the gas and to distillation, is converted into pitch, which at the high temperature of the main (350° Fahr.) is liquid. By regulating the amount of tar added and run off, a soft or hard pitch may be obtained free from ammonium chloride. Obviously tar fog carrying free carbon will pass from the collecting main to the condensing system, and so the whole pitch fraction will not be obtained. Undoubtedly, however, a distinct pitch fraction is produced. It will be noticed that the temperature in the Dessau main (350° Fahr.) is much below the final temperatures obtaining in tar-stills, and so the proces is more one of exaporation than distillation. In my opinion, Dr. Davidson's collecting-main method of producing the pitch fraction is superior to Feld's.

In the "Cava" process of tar distillation the highest temperature to which the tar is subjected is from 200° to 250° C., according to whether a soft or a hard pitch is required; and the distillation—or, more correctly, evaporation—is effected by passing heated air over the tar contained in a horizontal retort. Blades mounted on a revolving central shaft plunge into the tar and expose thin layers of it to the oxidizing and evaporating action of the brisk current of air. Some of the lighter products are oxidized, and so the amount of the bituminous substances in the pitch increases and likewise the yield of pitch; and it is claimed that on acount of the low working temperature there is no increase in free carbon. The evaporated products are condensed and treated in the usual way. Dr. Davidson's method involves at least the principle of the "Cava" process; but the separation of the tar products is limited to the pitch fraction, and this is not quite all recovered.

For complete direct fractionation of the tar within the condensing system, and also the evaporation and fractionation of a further quantity of crude tar by means of the sensible heat of the crude gas, I suggest the following method, using the plant in the accompanying illustration. Briefly, the method is as follows: The crude gas from the collecting main passes by the pipe *A* and the foul main *B* to the scrubber *C*. Here the gas is scrubbed by a screen of anthracene oil containing some pitch; and all the tar fog containing the free carbon is removed. The oil, etc., collecting in the receiver below flows to the pump *D*, to be recirculated; and there is also a continuous flow of the oil into the collecting main. The amount passing would be just what is necessary to maintain the bulk in the main, which would tend to decrease by the removal of pitch at *E*, and by evaporation. The gas passing *C*, after further partial cooling, is scrubbed in *F* for the removal of anthracene oil. The oil collecting in the receiver here is circulated by the pump *G*, and all the surplus flows to the pot *H*, and from there to storage, enough going to the pump *D* to keep up the bulk in the first scrubbing system, which would tend to be reduced by flow into the main, and by evaporation. Several fractions, depending on the lowering of the temperature of the gas by successive stages, could still be separated; but the separation of only one more fraction above the water dew-point of the gas will be considered. After passing *F*, the gas is cooled in the down pipe *I* to its water dew-point, and all the fog is removed in the scrubber *J* by a spray of ammoniacal liquor. The tar oil collects in the receiver *K*, separates from the liquor, and flows to storage. The liquor remains in the circulating system. The gas, completely freed from tar fog, but still carrying all the water as vapor, is passed without further cooling through the direct-recovery saturator *L*, where the ammonia is removed. It is then quickly cooled in one section of *M*, and naphthalene removed in the other, collecting in the settling-tank beneath as crude crystals. The gas now passes through the exhauster and the usual creosote scrubbers for the recovery of benzol, etc.

As has been stated, the crude gas is successively cooled between the different scrubbing systems, partly by air cooling, but as far as possible, by externally applied counter-current flow of crude tar brought in from other carbonizing installations. This tar is forced by the pump *N* through the successive heat exchanges *O* into the foul main at its highest point *P*, and flows down against the crude gas, cooling it and being itself further heated. It would here yield up to the gas, the bulk of its lighter constituents, and finally reach the gas collecting main by the open tray *R*.

The work done in the "Cava" process and by Dr. Davidson shows how simple and practical it is to produce pitch in such a vessel as the collecting main; it is sometimes too easy. In both these methods the hot pitchy tar is kept mixed by mechanical agitators. This is not difficult in a short main such as is used with the Dessau retorts or in the "Cava" still which is about 10 feet 8 inches in length; but when dealing with (say) a 60-oven coking plant, having a collecting main about 200 feet long, it is quite a different matter. To obtain the necessary agitation here several jets of high pressure steam blowing into the body of the liquid tar would be effective. Very little steam would be required, and after doing its work would pass away with the gas and be finally condensed.

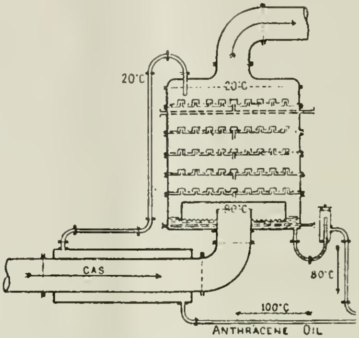
The gas leaving the collecting main of a coke oven installation may reach 300° C. The temperature to which the gas must be reduced before reaching the first scrubber is about 150° to 170° C.—a reduction would be largely effected by the crude tar entering the foul main at *P*, partly by external air. It would probably be advantageous to lag these mains, and use all the sensible heat of the gas for heating and evaporating added tar. The oil from the first scrubber, flowing in by the sluice valve *S*, mixes with the highly heated tar in the collecting main.

From the conditions of working, the tar in the collecting main would consist almost solely of pitch and anthracene oil, and in flowing to the outlet weir-valve *E* would be evaporated by the heat of the crude gas till only pitch remained. By regulating the flow from *E*, a soft or a hard pitch would be obtained. The crude gas, carrying as fog a portion of the pitch hydrocarbons and free carbon, would be cleaned in the first scrubber with oil at a temperature somewhat below the dew point temperature of the gas with regard to the lowest boiling compound of the pitch fraction. The gas temperature would vary with the conditions of carbonizing, with the nature of the pitch required, and with the amount of added tar evaporated. Without added tar, it would probably be about 150° C.; with added tar, however, the dew-point temperature would rise, corresponding to the richness of the added tar in the lower boiling point members of the pitch fraction required. It is quite possible, therefore, that the proper working temperature at this point would vary by 20° or 30° C. between the conditions of working hard pitch with added tar and soft pitch without added tar. The lowest temperature at which this section could be worked would be that which would just maintain the oil level in the receiver.

The type of scrubber proposed for cleaning the gas here is the Otto spray, but using instead of crude tar the fraction here collected. A large proportion of the pitch fraction is deposited from the gas in the collecting main, and the balance would be extracted in the first scrubber. This balance dissolves in the scrubbing oil and flows continuously into the collecting main. With these conditions the pitch fog is removed—not with the pitch fraction itself, but with a solution of a portion of the same dissolved in anthracence oil. This oil when sprayed through the gas in the scrubber would be partly evaporated and collected in the next scrubbing section. The temperature of the gas is lowered by this evaporation, and more fog is produced. But I have determined by experiment that the bulk of this fog goes forward with the gas. The time during which the fog remains in the spray after its formation is too short for the drops to get big enough for extraction. The oil carrying the pitch into the collecting main is evaporated, and comes down again in the condensing system. There is thus a continuous circulation of anthracence oil carrying the balance of the pitch fraction back to the collecting main. An issuing pressure of 20 pounds per square inch would be sufficient in the first scrubber; this pressure being raised in a pump of the "Albany" or the "Drum" type.

The gas from the first scrubber is now cooled as explained above to the dew-point temperature for the anthracene oil fraction, and scrubbed with this oil. The oil flows through the pot *H* to the storage. Since the pot is connected to the inlet of the first scrubber pump, the oil will naturally keep up the bulk in the first section. In this way the temperature of the scrubbing oil in the first scrubber will be lower than the temperature of the gas which it has to clean. As the temperature falls, I have found the fog which is produced more and more difficult to extract. But I consider a spray pressure of 30 pounds per square inch would be sufficient in this section. The extraction temperature here would likewise vary with the carbonizing conditions, but would be somewhat over 100° C.

The gas now enters the down pipe *I* at a temperature of at least a few degrees above the temperature at which ammonium chloride deposits occur—about 93° C. It is cooled by the external counter-current flow of tar as already described and also by ammoniacal liquor sprayed into it, which dissolves the ammonium chloride formed and so prevents deposits of the salt. The liquor returns to the receiver by the sealed dip-pipe. In cooling the gas it will become itself heated above the working temperature, and this is corrected in the heat exchanger. The gas, now cooled to its dew-point with regard to water, is scrubbed in *J* by a jet of ammoniacal liquor at about 90 pounds per square inch pressure. This high pressure is necessary to extract the lightest fog. For the first two sections, the Otto spray scrubber was suggested, and the method of operation is very similar to the usual practice—using, however, different scrubbing fluids. For the third section, in order to utilize the work done on the gas by the high pressure jet, I think that the best type of scrubber would be one designed on similar lines to the Körting ejector condenser. This would reduce considerably the work to be done by the exhauster. In the receiver *K* the tar oil would separate from the scrubbing liquor, and float on top of it, finally passing away by the overflow to the storage as a heavy creosote oil. The liquor would remain in the circulating system.



Naphthalene Washer.

During the past year or two, I have made on the Auchengeich direct-recovery plant a number of experiments with the Otto spray tar extractor, and using creosote oil, liquor, and tar and liquor mixed, at varying temperatures, I have obtained efficient tar extraction. The most important point is to ensure that the fog which is to be extracted is present in the gas before it reaches the scrubber. The extraction temperature in this section would be from 70° to 80° C. according to the carbonizing conditions. From this point the gas is treated in normal direct-recovery manner. For instance, it is first freed from ammonia in the direct-recovery saturator *L*, and then naphthalene is removed in (say) an Otto water spray naphthalene extractor *M*. The gas is then forced by the exhausters through the usual creosote scrubbers to recover the light oils. If the gas was required for town lighting, however, purifiers would take the place of the creosote scrubbers. In this particular case, it is to be remembered that the gas would be saturated with naphthalene vapor, and any fall of temperature would cause a deposition.

The content of naphthalene could be reduced by anthracene oil in the following way, using the plant here shown diagramatically.

The cooled gas, or a proportion of the total bulk, after being heated to 80° C., passes into the bottom chamber of a washer similar in principle to the Young and Aitken analyzer. Exhaust steam, or the sensible heat of the recovered tar fractions, or both, could be used for heating. A heat exchanger is shown in which the washing oil is cooled from its recovery temperature to that of the gas, the gas being itself partly heated. The cooled anthracene oil fills each of the trays up to the level of the overflow and runs through the washer in a continuous stream. In the bottom of the washer the oil is maintained by means of a steam coil at 80° C., at which temperature it leaves the washer. At 80° C. the anthracene oil cannot dissolve benzene, and, in fact, so far as examination of direct recovery tar extracted at this temperature indicates, very little solvent naphtha is removed from the gas. This is, no doubt, due to the fact that the light oil vapors are far from saturating the warm gas. It is quite likely, therefore, that such a washer could be operated considerably below 80° C. without any material effect on the benzene content in the gas; the lowest practical temperature could be found only by experiment. This oil outlet temperature being much below the boiling point of naphthalene, the anthracene oil will dissolve some of this hydrocarbon. The cold anthracene oil falling from tray to tray will be heated by the gas to 80° C. and the gas cooled. To ensure the gas being in contact with the oil at atmospheric temperature in the final tray a cold water coil is placed in the gas space under the top tray. When the oil in the washer is saturated with benzene either by admixture or by extraction from the gas, no further action on the benzene in the gas can take place.

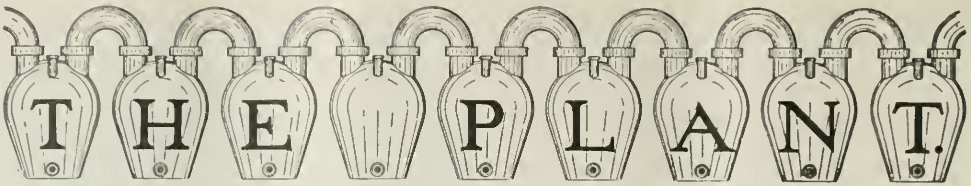
Referring again to the larger diagram, the plant from the third scrubber on is already applied in the direct ammonia recovery process, so that only the part between the collecting main and this third scrubber which is added to the ordinary direct ammonia recovery plant for the fractionation of the tar. The cost of this addition, together with the plant for dealing with the in-brought tar, for an installation carbonizing 360 tons of coal per day, would probably not exceed £3,000, and would serve for the fractionation of all the tar produced and added. The in-brought tar which could be dealt with might possibly reach 75% of that produced from the coal carbonized. The main attendants already required on such a coking installation could look after the two extra pumping sets, etc. The storage tanks required would be the same as those used in a tar distillery of the same capacity.

On account of the increased demand for benzene and toluene at the present time, there is added interest in the fractional method of recovering the tar products. In the ordinary condensing practice these products are divided between the tar and the cooled gas; so that, to recover the whole of each, washing of the gas and also distillation of the tar must be resorted to. With direct fractionation, only one operation—the washing of the gas—is required. Anything tending to increase the output of toluene, either by better recovery methods or by increased production per ton of coal carbonized, is highly desirable now, not only on account of the better financial return, but also on account of national needs. The required conditions in carbonizing would seem to be such as would give a high partial pressure of methane at the moment of destructive distillation. From some experiments I have made on ammonia production in bulk carbonization, I consider the ratio of toluene to benzene produced will follow the yield of ammonia.

CONCLUSION.

I have endeavored to show that, in many of the special methods applied for the extraction of the tar, fractional separation has been an underlying factor. The condition "that the tar should leave contact with the gas only at such a temperature that it could not dissolve the light oils," which Mr. Young stated in 1876, is fulfilled in direct tar fractionation. Mr. Young abandoned the principle of the Young and Aitken process on account of the trouble with the condensers, etc., due to the greater amount of naphthalene produced in later carbonizing practice; but, as I have already indicated, an extended application of this principle, using naphthalene-free anthracene oil, would overcome the difficulty. I consider that the method advocated by William Young so many years ago is still the correct one for gas works condensation practice, and particularly so with carbonization in continuous vertical retorts. In a number of works using these retorts, surprisingly low candle power of the gas has been found, on account of the light tar fog persisting with the gas till almost the final stages of cooling, and so removing from it illuminating hydrocarbons.

The production of cotton in Colombia is limited, and is practically confined to the Departments of Bolivar, Atlantico, and Magdalena. Some of this cotton is used in the local mills and a small quantity in other parts of the country. It resembles Sea Island cotton, but its fiber, which is long and silky, is said to be much too fine for use in the local manufacture of ordinary drill. This has resulted in the exportation of Colombian cotton to England and the importation of American staple to be used in domestic manufacture. This consulate is informed that the shipments to England brought as high as 24 cts. a pound.



CLEANING AND PLATING IN THE SAME SOLUTION.*

By **OLIVER P. WATTS.**

For a number of years past the electric current has been extensively used for removing grease and dirt from metals after polishing, and as a preliminary to electro-plating. From this use of the electric current for the successive operations of cleaning and plating metals, it was but a short step, in thought at least, to combine the two operations, and perform the cleaning and plating simultaneously in a single solution. Since its inception seven or eight years ago, this process has been steadily increasing in favor among platers, until today it is very widely practiced. Although the combined cleaning and plating solution is sometimes employed to produce the final deposit, its most frequent use is for giving to iron and steel a preliminary coating of copper before nickeling.

For this latter purpose it possesses great advantages over the use of two separate solutions. Not only is there a saving of the time and labor required to transfer the articles from one solution to the other, but any failure to remove the grease is detected while the object is still in the cleaning solution, by the failure of the copper to completely cover the iron.

Since the copper deposit needed for this purpose is very thin, the low current efficiency of the combined cleaning and plating solution is no drawback to its use. When, however, a heavy deposit of metal is desired, it is a different matter. Effective action by an electric cleaner requires an extremely rapid evolution of gas on the object which is being cleaned. But a plating solution in which much gas is evolved at the cathode has of necessity a low current efficiency of metal deposition. On the other hand, the fact that a portion of the current is used in depositing metal makes the cleaning less effective than it would be in the regular electric cleaner. There is therefore a possibility, at least, that the saving in handling consequent upon the use of the combined cleaner and plater may be more than counter-balanced by the loss in time and increased power cost when heavy deposits of metal are desired. A complete solution of this question can only be obtained in commercial establishments, but it is hoped that the author's laboratory experiments, and the limited conclusions which can be drawn from them may prove of interest, and may lead to investigations of this subject by practical platers.

E. G. Lovering,[1] using a combined cleaning and plating solution, claims that he obtains in 20 minutes a deposit of brass 0.002 to 0.003 inch thick, which would require two hours in the regular brass bath. He gives the following as the composition of his solution:

	Per liter.
½ lb. H. V. W.'s XXX lye	60 g.
2 oz. copper carbonate	15 g.
2 oz. zinc carbonate	15 g.
4 oz. ammonium carbonate	30 g.
4 oz. potassium cyanide	30 g.
1 gallon water	1000 cc.

For a copper solution he uses the same without the zinc carbonate, and claims to obtain a deposit 0.009 inch thick in fifteen minutes, doing in one tank an amount of work which formerly required three tanks. The solutions are used at boiling temperatures.

For comparison with Lovering's solution two ready-prepared compounds were purchased. One of them, for cleaning and depositing copper, will be referred to as *X*, the other, for cleaning and depositing brass, will be known as *Y*.

COPPER.

Cleaner "*X*," consisting of a fine white powder, evidently a mixture of caustic soda with other materials, was dissolved in water to form a solution containing 175 g. of solids in 1 liter of water. Although this solution is sold as a cold cleaner and plater, in order to do it justice in comparison with Lovering's solution it was also used hot. Copper electrodes of equal size were used except where the current densities quoted show anode and cathode to have been of unequal areas. Current efficiencies were determined by comparing the weight of copper deposited with that obtained from an Oettel copper coulometer connected in series with the plating solution. Since copper has a valence of one in cyanide solutions, at 100 per cent efficiency the weight of copper deposited should be twice that deposited in the coulometer. All current efficiencies for copper have been calculated on this basis.

The results of experiments with cleaner *X* are given in Tables I and II.

TABLE 1.

			Cathode					
			Current density.					
	Temperature.		Amp. per			Time.		
No.	C.	F.	sq. dm.	sq. ft.	Efficiency.	min.	Deposit.	Anode.
1	24.5	76	4.	37.3	11.4	60	Fine	Black
2	24.5	76	1.8	16.7	20.6	30	Fine	Black
3	50.	122	2.1	19.5	39.1	30	Good	Black

There was a vigorous evolution of gas at the cathode, but none at the anode, which was soon covered with a black coating, probably cupric oxide. The cathodes consisted of sheet brass coated with grease from the polishing wheels, and received deposits which were perfect in continuity and adherence. A comparison of experiments 1 and 2 shows a considerable increase in efficiency as the result of diminishing the current density, and experiment 3 gives a still greater efficiency as the result of heating the solution. The polarization was 1.3 volts.

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*Paper prepared for the 27th general meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22-24, 1915.

[1] Metal Industry, 1913, p. 173.

TABLE II.

			Cathode			Anode			
			Current density.			Current density.			
	Temp.		sq.	sq.	Effi-	sq.	sq.	Effi-	
No.	C.	F.	dm.	ft.	ciency.	dm.	ft.	ciency.	Anode.
4	71	160	7.9	73.5	17.3	5.1	47.4	—3.5	Black
5	70	158	7.9	73.5	16.6	5.1	47.4	—2.4	Black
6	70	158	7.5	70.0	13.8	4.6	43.0	—0.5	Black
7	70	158	1.9	17.7	35.5	1.1	10.2	...	Black
8	70	158	7.0	65.0	14.7	4.6	43.0	4.7	Nearly clean
9	70	158	7.0	65.0	13.3	4.6	43.0	2.7	Clean and bright

Table II shows the effect of the addition of a small amount of potassium cyanide in the hope of dissolving the black film on the anode. The time of deposition was 30 minutes.

The only effect of the addition of cyanide was an improvement in the color and brightness of the deposit. The negative sign before anode efficiencies indicates a gain instead of a loss in weight. In No. 8 an addition of 25 grams per liter of Rochelle salt was made in the hope of inducing corrosion of the anode, and in No. 9 this was increased to 35 grams, with the gratifying result that the black film no longer formed on the anode, although the efficiency of corrosion was still far from satisfactory. It is evident that in order to secure good anode corrosion it will be necessary to lower the current density, add more tartrate, or possibly do both. The previous polarization of 1.3 was unchanged by this addition of the Rochelle salt.

Lovering's solution was next tried. In making this, the zinc carbonate of the formula quoted was replaced by copper carbonate, giving a total of 30 grams per liter of the latter. It was then found necessary to use 70 grams of sodium cyanide instead of 30 grams of potassium cyanide to dissolve the copper carbonate. Tests of this solution are given in Table III.

TABLE III.

			—Current density—		
	Temperature.		Amperes	Amperes	Efficiency.
No.	C.	F.	per sq. dm.	per sq. ft.	per cent.
10	25	77	3.9	36.3	22.1
11	25	77	1.8	16.7	47.6
12	99	210	3.5	32.5	99.4

At room temperature this solution showed a much higher efficiency of deposition than cleaner *X*, but the anode was entirely black. To improve anode corrrosion 20 grams of tartaric acid and 20 cc. of strong ammonia were added. At the same time it was found necessary to add a small amount of sodium cyanide to completely discharge the blue color of the solution. The result of these changes in the electrolyte and the use of half the former current density is shown in No. 11. In spite of doubling the current density in No. 12, which should lower the efficiency, other conditions remaining unchanged, elevation of the temperature to gentle boiling has caused a rise in efficiency to practically 100 per cent. Under the conditions of No. 12 this solution would not act as an effective cleaner unless a large amount of sodium cyanide were added.

Since the combined cleaner and plater may be considered as only an ordinary cyanide copper solution to which lye has been added, it was considered interesting to compare Lovering's solution with another bath of the same composition except that the lye was left out. A solution was made up of the following composition:

Ammonium carbonate	40 grams
Copper carbonate	36 grams
Sodium cyanide	36 grams
Water	1000 cc.

Tests of this solution *(L)* in comparison with the same to which 50 grams per liter of caustic soda was added *(LA)* are given for 30 minutes of deposition in Table IV.

TABLE IV.

			Cathode			Anode		
	Temp.		Current density.		Effi-	Current density.		Effi-
No.	C.	F.	Sq. dm.	Sq. ft.	ciency.	Sq. dm.	Sq. ft.	ciency.
13*L*	99	210	4.2	39.0	97.4	...	....	....
14*LA*	99	210	3.8	35.3	96.7	...	....	....
15*L*	80	176	2.6	24.2	88.6	...	....	....
16*LA*	80	176	2.9	26.9	85.2	...	....	....
17*L*	30	86	3.6	33.5	30.6	2.8	26.0	26.7
18*L*	82	180	3.8	36.3	86.2	3.0	27.9	80.9
19*LA*	82	180	2.8	26.0	84.9	2.7	25.4	15.7
20*L*	25	77	2.2	20.4	49.4	3.0	27.9	51.7
21*L*	25	77	2.5	23.1	34.0	3.0	27.9	34.0

A comparison of 13 and 14 shows that the addition of caustic soda has no effect upon the efficiency of deposition, but the formation of films on the anodes showed the need of more cyanide, and 5 grams per liter of sodium cyanide was added to each solution. This addition is partly responsible for the lower efficiencies of 15 and 16, the other factor in lowering the efficiency being the fall in temperature. On the other hand the lowering of the current density must have tended in the opposite direction. A comparison of 17 and 18 shows the remarkable effect of temperature upon the current efficiency at each electrode. It has previously been pointed out that elevation of temperature permits the use of unprecedented current densities in nickel plating also.[2] The cause of this greatly stimulating effect of heat upon electrodeposition appears to lie in an increase in the rate of diffusion of dissolved substances with rise of temperature, and the increased circulation of the liquid as a whole, caused by convection currents. To test the effect of artificial circulation upon current efficiency two cells containing the same solution were connected in series so that the same current traversed both, and a stirrer rotated at 1,000 r. p. m. was placed in one cell. The results are shown in 20 and 21, the former containing the stirrer. Since stirring prevents the film of solution in contact with the cathode from becoming depleted in metal it was to be expected that the efficiency of deposition would be increasefd by stirring. Whenever the current efficiency in a stationary solution is greatly below 100 per cent, stirring ought to increase the efficiency, except when the electrolyte contains some corrosive substance such as ferric chloride or an acid, which vigorously attacks the cathode. A comparison of anode and cathode efficiencies for solution *L* shows a very satisfactory state of affairs, as the anode supplies metal at the same rate at which it is deposited. In *LA*, however, the anode was entirely black and corroded so poorly that for long continued use it would be necessary to supply metal by the addition of copper carbonate or cyanide.

It has been stated by Brown and Mathers[3] that the current efficiency of Weil's solution, consisting of copper sulphate, Rochelle salt and caustic soda, is 100 per cent at both electrodes for current densities not exceeding 1 ampere per square decimeter. This suggested to the writer the addition of a tartrate for the purpose of increasing the anode corrosion.

To study the effect of a tartrate upon anode corrosion solution *LA* was digested with excess of copper carbonate to remove the free cyanide and divided into two portions, to one of which *(LAT)*, 60 grams per liter of soduim potassium tartrate was added. Tests of these solutions appear in Table V.

TABLE V.

			Cathode			Anode		
	Temp.		Current density.		Effi-	Current density.		Effi-
No.	C.	F.	Sq.dm.	Sq. ft.	ciency.	Sq.dm.	Sq. ft.	ciency.
22*LA*	71	160	6.6	61.2	33.9	5.1	47.4	3.6
23*LAT*	71	160	6.0	55.8	35.9	6.1	56.7	55.7
24*LA*	71	160	6.6	61.2	47.3	5.1	47.1	6.7
25*LAT*	71	160	6.0	55.8	67.3	6.1	56.7	62.2
26*LA*	71	160	7.7	71.6	26.8	5.1	47.1	9.4
27*LAT*	71	160	6.6	61.2	55.1	6.1	56.7	57.1
28*LA*	99	210	7.7	71.6	79.0	5.1	47.1	39.0
29*LAT*	100	212	6.6	61.2	97.5	6.1	56.7	100.5
30*W*	70	158	6.8	63.2	28.4	4.0	37.2	0.3
31*WCy*	71	160	6.2	57.7	52.1	4.2	39.0	39.7

These tests were made with the two solutions, one without, and one with the addition of the tartrate, connected in series. Nos. 22 and 23 indicated a lack of free cyanide, and 2 grams per liter of sodium was added to each solution for tests 24 and 25. For tests 26 to 29, inclusive, the amount of free cyanide was increased to 6 grams per liter. The first addition of free cyanide to *LA* caused an increase in the efficiency of deposition, as well as in anode corrosion; a still further increase in cyanide gave the lessened efficiency at the cathode which had been expected for the first addition. In all tests of *LA* a black coating, probably cupric oxide, formed on the anode, and the corrosion of the anode was absolutely unsatisfactory. The behavior of the anode in *LAT* was in striking contrast to this. As seen in the table, its corrosion was closely proportional to deposition at the cathode, and it remained bright and free from any film of oxide or cyanide.

The effect of heating these solutions to boiling was no less striking in 28 and 29 than previously in 12, 13 and 14. In 29 the amount of tartrate had been increased to 110 grams per liter.

To learn more definitely the parts played by the cyanide and the tartrate in producing the very satisfactory operation of solution *LAT*, Weil's bath, was made up as follows:[4]

Copper sulphate	60 grams
Sodium hydrate (lye)	50 grams
Sodium potassium tartrate	160 grams
Water	1000 cc.

To one portion of this *(WCy)* 30 grams per liter of sodium cyanide was added, just enough to discharge the deep-blue color of the original solution. These two solutions, 30 and 31, were then electrolized in series. The nature of the deposited copper, as well as the current efficiency, indicated that more cyanide was needed in *WCy*, while 30 shows that the tartrate without cyanide does not make a satisfactory solution, for combined cleaning and plating, for it is necessary to use a very high current density in order to cut down the cathode efficiency sufficiently for effective cleaning, and this reduces the anode efficiency nearly to zero.

Two experiments to determine the thickness of metal deposited in a half-hour from the boiling solution *LAT*, at 9 amperes per square decimeter or 84 amperes per square foot, gave 0.0042 in. at a current efficiency of 88.8 per cent. At this rate of deposition 1 hour and 4 minutes would have been required for a deposit 0.009 in. thick, such as Lovering obtained in 15 minutes, and a current density of 360 amperes per square foot would have been needed to give this deposit in 15 minutes at the current efficiency of these experiments.

These solutions yielded bright, fine-looking deposits, which gave no indication of stripping from the greasy sheet metal on which the copper was deposited. This must not be taken as an indorsement of the use of these solutions for plating objects with crevices or deep cavities, as no such articles were available for testing.

Cleaner *X* is only suitable for preliminary plating which is to be followed by the deposition of a heavier coating from another solution.

Lovering's solution is capable of doing effective cleaning on flat metal, and will when boiling deposit copper more rapidly than the cold copper sulphate bath, as it permits the use of higher current densities than the latter. In this connection it should be noted that at 50 per cent efficiency for the cyanide bath the deposit of copper equals that by the same current at 100 per cent efficiency for the copper sulphate solution.

For effective cleaning it is possible that the current efficiency ought not to be allowed to exceed 50 per cent and a high current density must be used.

The hotter the solution the more effective the cleaning, and the higher the current density which may be used without producing a bad deposit.

The proportions of the total current devoted to cleaning and to plating may be controlled by adjustment of the temperature, the amount of copper in the bath, the current density, and the amount of free cyanide present. An increase in the first two, and a diminution of the last two increases the per cent of the total

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[2] Brass World, 1915, p. 34.
[3] J. Phys. Chem., 10, 51.

[4] J. Phys. Chem., 10, 51.

current which is devoted to the deposition of metal, and *vice versa*.

The addition of 60 to 75 grams per liter (8 to 10 ounces per gallon) of Rochelle salt or other tartrate to Lovering's bath greatly improves the operation of its solution.

BRASS.

A first attempt to clean metal and deposit brass was made with cleaner "Y," already referred to. A solution containing 175 grams of the powder per liter evolved much gas, and gave only a very thin deposit looking like pure copper at 71° C. and a current density of 6 amperes per square decimeter. As this is supposed to be used cold, it was also tried at 20° C. with current densities of 3 and 6 amperes per square decimeter. A very thin deposit of red brass was obtained. The solution cleaned the metal, but did not give a satisfactory deposit of brass.

Lovering's brass solution was made up according to the formula previously given, except that more potassium cyanide was needed to secure solution. As the color of the brass deposited from this was not satisfactory, additions of copper and zinc carbonates and sodium cyanide were made, until finally a good color was obtained between 70° and 90° C. The deposits adhered firmly upon sheet metal covered with grease from the polishing wheels, but thick deposits, equivalent to 15 minutes at 8 amperes per square decimeter, were hard and rather brittle, cracking when the sheet was bent at right angles. No attempt was made to determine current efficiencies. One interesting observation was that the addition of 50 grams per liter of lye to a hot brass plating solution which was depositing brass of an excellent color, caused the color of the deposit to change to that of pure zinc.

The few experiments tried with the brass solution show that brass may be deposited from a combined cleaning and plating solution in a manner similar to copper, but on account of the difficulty of satisfactorily controlling the color of the deposit, the whole matter has been made the subject of a more complete investigation, which is now being carried on in the electrochemical laboratories of the University.

NICKEL.

Since the combined cleaning and plating solution for copper is most extensively used as a preliminary to nickeling iron and steel, it was thought that a solution for the simultaneous cleaning and nickeling of iron might be of value to the plating industry. The experiments so far tried for the purpose have failed. What is needed is an alkaline nickel solution which at or near the boiling point will give a smooth deposit of nickel at a current density of 30 to 50 amperes per square foot, at a current efficiency between 30 and 50 per cent.

Naturally cyanide solutions were first tried. A boiling solution containing 70 grams per liter of nickel sulphate in the least amount of potassium cyanide that would dissolve the precipitate gave a bright and adherent deposit of nickel on greasy metal, but the efficiency of deposition proved to be only 0.05 per cent. The addition of caustic potash did not improve matters, nor did the substitution of nickel carbonate for the sulphate. The cyanide solution was abandoned, and an attempt was made to hold the nickel in solution by other means. Tartrates prevented the precipitation of nickel by alkalies in cold solutions, but when heated the nickel was precipitated. Experiments are still in progress upon this interesting, but seemingly difficult problem.

The most important result of these experiments is the great improvement in anode corrosion caused by the addition of a tartrate to the copper solution. Other deductions of less importance are to be found at the close of the section on copper.

PROGRESS IN PAPERMAKING CHEMISTRY.*

By PROF. RALPH H. McKEE.

In the knowledge that the supply of pulp woods used at present is limited, and that about twenty years hence the great bulk of paper made in this country will have to be produced from other fibers than those used now, many workers are interested and working on materials that are likely to prove acceptable as surrogates or substitutes for spruce and other woods.

Solutions of the problem that confronts us fall into two classes: the first is where trees formerly considered inferior are found with slight modification of treatment to give fair quality fiber for news and other inexpensive paper, thereby conserving the more valuable woods for use for chemical pulp. The Forest Products Laboratory has done much valuable work along this line and mills are beginning to see the use of tamarack, jack pines, Douglas fir and other similar woods.

The second solution lies in the use of waste fibrous materials or crop plants as papermaking material. There is every reason to believe that the enormous, quantities of waste flax straw in the North Central States and of cotton seed hull fiber in the South will soon be made to yield a large tonnage to take the place of rag fiber. As substitutes for wood, sisal waste and sugar cane fiber deserve to be considered, but the large tonnage will have to be supplied from planted materials, partly by reforestation, but more largely by quick growing woody materials not now much used. The two materials that promise most in this respect are bamboo in the south and hemp in the north. One northern mill by acreage planting trials conducted several years ago, reached the conclusion that when wood reached $12 a cord, then it would pay to plant hemp as a source of fiber. From present wood prices, we shall not have to wait long before hemp will be in the digesters.

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*From a paper read before the Technical Division of the American Paper and Pulp Association at the annual meeting in New York, Feb. 19, 1915.

UTILIZATION OF PULP WASTE.

Pulp mill waste is giving increasing trouble to water-courses. The waste from mechanical and soda pulp mills is comparatively harmless but that from the sulphite pulp mills is ordinarily considered undesirable and is being legislated against.

The methods tried for its disposal are in four groups —namely, irrigation, artificial biologic treatment, infiltration and evaporation. The first three yield no return and can only be applied when the climatic and soil conditions at the mill are favorable. Evaporation is too expensive unless the partly evaporated material can be used for tanning, coal briquet binder, on roads as a dust preventive in competition with oil, or in some other manner.

WASTE SULPHITE LIQUOR.

The earlier promises of the use of sulphite waste as a true tanning material are now thought to be largely without basis; all it seems to do is to serve as a partial substitute for weighting materials like glucose. A use may be found for waste sulphite liquor as a briquetting binder for coal slack, but the method has not yet been adequately developed and price of coal is still too cheap in this country to make briquetting of coal slack interesting from a business standpoint. As a dust preventive, waste sulphite liquor is satisfactory but with its large content of water, freight charges prevent it being shipped any considerable distance from the mill.

A really satisfactory solution of the sulphite waste problem is yet to be found. The transformation of the glucose content of the liquor into alcohol, a process by which three Swedish mills are making about a million and a quarter gallons of alcohol a year seems most promising. Two mills in this country are now producing alcohol from waste sulphite liquor. The yield is ordinarily about 15 gallons of 95 per cent alcohol, a ton of sulphite pulp, but under the best conditions, it is said to be possible to increase this to fully twenty-five gallons a ton of pulp. However, the slops, after the alcohol extraction, are fully as objectionable as the original waste liquor.

NEW PULP PROCESSES.

Of the new pulp processes, the König process, using successive treatments with 4 per cent ammonia and 0.5 per cent sulphuric acid, gives about the same yield of pulp as ordinary methods, but the byproducts of alcohol and rosin are of much more value. It is also said that the cooking liquor after use has value as a cattle food.

Success of this process seems to depend largely if not entirely on a decrease in the price of ammonia and the successful use of the byproduct as a fodder. In this connection, it should be said that it is very probable that Haber's ammonia synthesis from hydrogen and nitrogen gases, commercially developed by one of the large German chemical companies, is destined to lower considerably, the price of ammonia.

THE USE OF LIQUID SULPHUR DIOXIDE.

Efforts are being continually made to increase the amount of free acid in the sulphite digester. Patents have lately been taken out by Messrs. Wolf and Moore of the Burgess Sulphite Company for a scheme whereby gas from liquefied sulphur dioxide is forced into the digester after filling and injecting steam.

THE DYESTUFFS QUESTION.

The coal tar dye situation in this country is bad, but there seems little immediate help in sight. Importations are coming in, but not in large amounts. American dye makers are in a position to make only a minor part of the tonnage of dyes needed by American papermakers and if importation should cease, the stocks on hand would soon vanish. Many papermakers are conserving their stocks by declining orders for intensely colored papers and issuing only whites and tints that require but small amounts of dyes. Steps can be taken to obtain in the future an American source of most dyes but to do so the price will have to be paid, and I doubt if the paper industry is willing to pay its share.

HIGH BLEACHING COSTS.

Much as I would like to, the time at my disposal does not permit me to discuss several other questions which deserve your consideration such as the excessively high bleaching costs of many American pulp mills, the equally high losses in steam and chemicals of many soda mills, and the still greater monetary losses in many mills due to fiber being allowed to go out with the waste water into the river.

In asking me to speak before the Technical Division Mr. Bishop asked me to offer suggestions as to what might be accomplished by such a division.

THE FORMATION OF A TECHNICAL DIVISION.

Before touching this question, allow me to offer my congratulations to the men here gathered together. This meeting and the organization of this division, promises to do more towards putting this industry on a sound and paying basis than any previous step made by the American paper and pulp industry. It is moreover, a pleasure to acknowledge that the advance nearest in importance to this, the getting of American mills to put in a cost system, was also largely aided by the initiative and pushing qualities of H. E. Fletcher, who suggested to President Moore the formation of this Technical Division of the American Paper and Pulp Association. The American paper and pulp industry owes Mr. Fletcher a vote of thanks for his work in making it possible for the members interested in the technical work of the mills to come together in this way for the discussion of common problems.

It has often been said "that there is active and substantial co-operation in every interest which in any manner touches the production and consumption of paper, except among the manufacturers themselves." The formation of this division promises more toward a change from the condition given in the quotation I have just read, if it is a true statement, than any other step that could be made. Men engaged in the production and scientific phases of mill work have much to gain and at no injury to the mills they represent, by attendance and discussion at such meetings.

SUGGESTIONS REGARDING THE SCOPE OF THE DIVISION.

Some subjects, which it seems to me should early be taken up are the following:

1—The paper manufacturer needs to be able to tell from a sample of a pound or less of pulp, what kind of a paper it will make, or whether in a given furnish, it will serve to give the desired standard quality of paper.

2—Standard definitions for the different grades of bleached and unbleached pulp.

Perhaps with this should go a standard or definition of excessive bleaching, as the evil effects of overbleaching on the paper are but rarely fully appreciated by the pulpmaker.

3—It is probable that a different unit in purchasing pulpwood would be to the mutual advantage of the woodowner and pulp mill. Certainly the mill should buy the wood for the pulp it will make, and the cord of 128 cubic feet does not measure that at all accurately. The cellulose content varies much with the quality of the wood, especially if calculated on the yield per volume cord of 128 cu. ft.; *e. g.*, sound spruce and balsam fir vary in yield from 16 to 24 per cent.

Twenty-five years ago, wood 8 ft. to 18 ft. in diameter cost $3 a cord at the mill; now, the actual content of the cord is less in that often half the wood will not be over 3 ft. in diameter. Then there was no need for accurate measurement of the wood; today, wood is expensive and accuracy is needed.

4—A discussion of the uses of byproducts. The mill dividends appear to be in the future largely linked with the use made of byproducts.

AN AMERICAN SCHOOL OF PAPER MAKING.

The Paper and Pulp School of the University of Maine, which I have the honor to represent, is interested in the same problems as this division, and to you it sends its greetings.

We are attempting to give young men the basic training for pulp and paper work, but we must look to you to give the opportunity for practical mill experience. Last summer, fifteen of the young men studying at Orono, worked in paper and pulp mills and received experience of the most valuable character. They worked where they were told, more as hands in the beaker room than anywhere else.

That the mills found the young men fully earned their $50 a month and were worth while, was indicated in several ways, *e. g.*, half the superintendents asked the young men to write to them with regard to a regular job, after graduation. Next summer, we will want to place twenty-five young men in the mills from June 15 to September 1. I hope you who are here present will aid in giving these young men an opportunity for practical mill experience the coming summer.

A LIBRARY OF PAPER MAKING CHEMISTRY AND ENGINEERING.

One of the needs of the industry in America is a library containing a practically complete collection of books and periodicals on paper and pulp, the volumes of which will be available for loan to those in the industry anywhere in the country who have need for information on these lines.

The University of Maine has now about half completed such a library but as yet has no facilities for the loaning of the books or the completion of the files. It is hoped that arrangements may be made with the American Pulp and Paper Association making such a loan possibility a reality and permitting the completion of the list of books and technical periodicals.

A little later, it is the intention of the Paper and Pulp School of the University of Maine, to issue bulletins on production, control and analytical methods of use to paper and pulp mills, and bibliographies on special subjects of interest to men working in the industry. It is my intention to see that each of you shall receive copies of these as issued and I trust you will find them of interest.

HEAT LOSSES FROM AN ELECTRIC STEEL FURNACE.*

By W. H. WILLS and A. H. SCHUYLER.

The furnace investigated is at the plant of the Treadwell Engineering Company, Easton, Pa., and has been already described in the Transactions of the American Electrochemical Society (1914) 25, p. 133, where a full description of the furnace with its dimensions may be found. The furnace is of two-ton rated capacity, with magnesite brick hearth overlaid with burnt dolomite. The pouring spout is in the center of the front side and at each side is a charging door. Three cylindrical graphite electrodes 8 inches (20 cm.) in diameter pass through the roof, threaded for continuous feeding, and are used in 180 pound (82 kg.) sections three feet (90 cm.) long. The power supply is 40 kw., 3 phase, 60 cycle, alternating current, the potential between the electrodes being 80 volts and the normal current per phase 2,500 to 3,000 amperes. The Easton Light and Power Company furnishes the current, at 11,000 volts on the primary.

The object of the experiments was:

I. To investigate the heat losses due to gases issuing from charging doors and tap holes.

II. To investigate the heat losses by conduction into the electrodes and by the water jackets surrounding the electrodes.

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*Paper presented at the 28th general meeting of the American Electrochemical Society, in San Francisco, Sept. 16-18, 1915.

The product is high grade steel castings, carbon 0.05 to 1.20. Raw material, boiler punchings and structural steel scrap. Lime and some hematite are charged as flux, with fluorspar later. Coke dust is added toward the end of the run, to deoxidize the slag. Final additions of ferro-manganese, ferro-silicon, and aluminium are made. The average length of the heat is 4½ hours. Electrode consumption per heat (2 tons) about 60 pounds (27 kg.); per ton of steel 30 pounds (13.6 kg.); per kw. hour 0.0375 pound (17 grams). The average power input during the test was 350 kw.

I. HEAT LOSSES THROUGH ESCAPING GASES.

Sheet iron flues to facilitate collection of the issuing gases and their measurement were fitted to the furnace doors and tap-hole. The one for the charging doors had a 6-inch pipe, and the one for the tap-hole a 3-inch pipe. The temperature of the escaping gases was measured as they issued by a LeChatelier thermocouple, protected by asbestos tubing. The temperature of the gases leaving the pipes, where the velocity was measured, was taken by suitable mercury thermometers. The velocity of the gases issuing from the 3-inch pipe was measured with 2½-inch (6 cm.) anemometer and on the 6-inch (7.5 cm.) pipes and with a 6-inch anemometer. An Orsat apparatus was used to analyze the escaping gases.

On the first test, run April 16, 1915, the length of the run was four hours twenty-five minutes. The sheet iron flues were placed over the charging door openings and tap hole, and carefully plastered around with fire clay. The following observations were taken at approximately equal intervals:

1. Temperature of gases escaping through the door and tap hole.
2. Temperature of gases leaving pipes.
3. Velocity of gases leaving pipes.
4. Power input to the furnace.
5. Samples and analysis of furnace gases.
6. Barometer reading.

In taking the temperature of the escaping gases, the hot junction of the thermocouple was placed at different points in the openings, and an average reading of the temperatures of gases escaping was obtained.

The following table gives a general log of the observations taken:

II. ELECTRODE HEAT LOSSES.

The furnace was provided with three electrodes passing through the roof of the furnace; each being in sections of about three feet long and weighing 180 pounds per section (82 kg.). In the electrode holders electrical connection is made by copper plates screwed fast against the graphite and connected to the bus bars by heavy stranded copper cables.

The tests on electrode heat losses were run on April 17, 1915, from 9:35 a. m. to 1:35 p. m. Two chalk marks were made on each electrode between the water jacket and the electrode holder. The temperature of the incoming and outgoing water for the electrode water jackets was measured with ordinary thermometers.

The following observations were taken every half hour:

1. Temperature on the electrode surface at each chalk mark.
2. Power input to the furnace.
3. Current passing through each electrode.
4. Temperature of cooling water entering and leaving water jackets.
5. Rate of discharge of cooling water.

The temperature of the electrode surface was taken by a thermocouple pressed by a small piece of asbestos tightly against the surface of the electrode. From these

TABLE I.

Time.	Initial Temperature of Gases, C.°	Temperature of Gases leaving Pipes, C.°	Velocity of Gases leaving Pipes. Feet per Minute.	Velocity of Gases leaving Pipes. Meters per Minute.	Power Input, Kw.
12:30	Furnace charged.				
1:30	door 1.....745	215	310	80	300
	door 2.....755	158	340	86	
	tap hole....716	202	300	76	
2:00	door 1.....755	230	295	75	390
	door 2.....723	142	290	73	
	tap hole....735	312	240	61	
2:30	door 1.....744	242	335	85	390
	door 2.....784	117	290	73	
	tap hole....735	256	260	66	
3:00	door 1.....842	255	320	81	350
	door 2.....832	110	256	65	
	tap hole....745	230	300	76	
3:15	door 1.....866	265	334	85	360
	door 2.....804	108	260	66	
	tap hole....876	192	288	73	
3:30	door 1.....903	270	325	82	350
	door 2.....850	110	245	62	
	tap hole....920	235	292	74	
4:00	door 1....1000	282	350	89	350
	door 2.....929	115	250	64	
	tap hole....973	195	300	76	
4:30	door 1....1018	210	370	94	370
	door 2.....964	112	255	65	
	tap hole...1010	203	284	72	
5:00	Furnace tapped.				

TABLE II.—ANALYSES OF GASES.

Time.	Opening.	CO_2	O_2	N_2
1:30	door 2	3.6	18.6	79.2
2:00	tap hole	1.8	9.4	78.8
2:30	door 2	0.4	20.2	79.4
2:50	tap hole	5.0	16.9	78.1
3:15	tap hole	3.0	18.1	78.9
4:00	door 1	3.2	14.9	81.9

TABLE III.—HEAT LOSSES.

Time.	Opening.	Corrected Vol. Escaping Gases per Minute, Cu. Meters.	Temp. C.°	Calories Lost per Minute.	Kw. Lost.	Total Loss, Kw.
1:30	door 1....	1.1	745	273.5	19.07	44.4
	door 2....	1.216	755	304.8	21.25	
	tap hole...	0.247	716	58.4	4.08	
2:00	door 1....	0.932	755	245.3	17.10	40.00
	door 2....	1.093	723	274.0	19.12	
	tap hole...	0.202	735	54.1	3.78	
2:30	door 1....	1.006	774	256.7	17.9	41.8
	door 2....	1.162	784	796.1	20.65	
	tap hole...	0.194	735	46.4	3.24	
3:00	door 1....	0.941	842	267.5	18.62	39.00
	door 2....	0.832	832	233.	16.27	
	tap hole...	0.233	745	58.1	4.06	
3:15	door 1....	0.961	866	277.8	19.38	44.40
	door 2....	0.073	804	288.1	20.10	
	tap hole...	0.242	876	70.7	4.93	
3:30	door 1....	0.930	903	288.9	19.64	44.40
	door 2....	1.010	850	285.3	19.92	
	tap hole...	0.225	920	69.4	4.84	
4:00	door 1....	0.975	1000	329.9	23.00	50.85
	door 2....	1.014	929	316.7	22.10	
	tap hole...	0.251	973	82.4	5.75	
4:30	door 1....	1.180	1018	406.9	28.37	57.50
	door 2....	1.038	964	337.7	23.55	
	tap hole...	0.234	1010	80.00	5.57	

observations the calories carried away from the electrode by the cooling water and by conduction through the electrodes could be calculated, using the heat conductivity of graphite for the range of temperature observed.

Table IV contains the record of water entering and leaving the cooling jackets and its quantity.

TABLE IV.—LOG OF COOLING WATER.

	Cooling Water			
			Quantity per Minute.	
Time.	Entering C.°	Leaving C.°	Lb.	Kg.
9:45 A. M.	8.5	17.5	42	19.05
10:40 A. M.	8.5	15.5	42	19.05
11:05 A. M.	8.5	16.0	42	19.05
11:30 A. M.	8.5	19.0	42	19.05
12:00 M.	8.5	20.5	40	18.15
12:30 P. M.	8.5	23.0	40	18.15
1:00 P. M.	8.5	25.5	42	19.05
1:30 P. M.	8.5	26.0	42	19.05

Furnace charged at 9:35 A. M.
Furnace poured at 1:35 P. M.

Table V shows the reduced values of heat losses in cooling water per minute at each of the 8 observations.

TABLE V.—HEAT LOSS IN WATER JACKETS.

Time.	Calories per Minute.	Kw.	Power Input.	Percentage Energy Loss.
9:45	171.45	11.95	200	5.97
10:40	133.35	9.3	360	2.58
11:05	14.28	9.97	375	2.66
11:30	200.	13.95	350	3.99
12:00	217.8	15.18	400	3.80
12:30	263.4	18.38	300	6.13
1:00	324.	22.6	300	7.53
1:30	334.	23.3	310	7.50
			Average	5.20

In Table VI t_1 is the temperature at the upper chalk mark, t_2 the temperature at the lower chalk mark, and the next column gives the difference in temperature in centigrade degrees, for each of the three electrodes, at the times given.

TABLE VI.—TEMPERATURE OBSERVATIONS ON ELECTRODES.

	Electrode No. 1.			Electrode No. 2.			Electrode No. 3.		
Time.	t_1	t_2	t_2-t_1	t_1	t_2	t_2-t_1	t_1	t_2	t_2-t_1
9:45 A. M.	208	293	85	230	304	74	230	304	74
10:40 A. M.	227	293	66	230	293	63	241	329	88
11:05 A.M.	241	316	75	241	293	52	251	329	78
11:30 A. M.	251	328	77	230	293	63	241	328	87
12:00 M.	251	328	77	241	305	64	251	334	83
12:30 P. M.	230	294	64	241	305	64	209	316	107
1:00 P. M.	241	305	64	251	328	77	262	360	98
1:30 P. M.	230	305	75	209	294	85	230	328	98

Table VII was calculated using the following data:

Cross section of each electrode 50.265 square inches (324 sq. cm.). Length of electrode between observation points, as follows:

	Electrode No. 1.	Electrode No. 2.	Electrode No. 3.
9:45 a. m. observations	8 inches (20 cm.)	7 inches (17.5 cm.)	7.5 inches (18.5 cm.)
Other observations	4.87 inches (12.2 cm.)	4.87 inches (12.2 cm.)	5.25 inches (13.1 cm.)

Electrical resistivity of the graphite assumed 0.0003325 ohms per inch cube.

Thermal conductivity of graphite assumed 3.71 watts per inch cube.

These values were assumed as average values for the range of temperature concerned.

From these data calculations of the flow of heat in kilowatts were made according to the methods of Carl Hering, Transactions of the American Institute of Electrical Engineers (1910) 29, 285, with the following results:

TABLE VII.

Time.	Electrode No. 1, Kw.	Electrode No. 2, Kw.	Electrode No. 3, Kw.	Total Kw.	Power input Kw.	Percentage of power input.
9:45	1.221	1.918	1.783	5.622	200	2.81
10:40	2.412	2.281	3.011	7.704	360	2.14
11:05	2.775	1.894	2.612	7.261	375	1.93
11:30	2.855	2.229	2.874	8.019	350	2.32
12:00	2.805	3.237	2.813	7.945	400	1.99
12:30	2.344	2.677	3.370	8.441	300	2.81
1:00	3.367	2.876	3.403	8.646	300	2.88
1:30	2.784	3.171	3.403	9.358	310	3.02
					Average	2.10

The following table gives the rate of total electrode loss, by cooling water and by conduction through the electrodes, and its percentage of the power input of the furnace:

TABLE VIII.

	Cooling water, Kw.	Electrodes, Kw.	Total Kw.	Power input, Kw.	Percentage loss.
I	11.95	5.622	17.572	200	8.79
II	9.30	7.704	17.004	360	4.75
III	9.97	7.261	17.231	375	4.60
IV	13.95	8.019	21.969	350	6.26
V	15.18	7.945	13.125	400	5.78
VI	18.38	8.441	26.821	300	8.94
VII	22.60	8.646	31.246	300	10.42
VIII	23.30	9.358	32.658	310	10.53
				Average	7.30

GENERAL REMARKS.

Both tests were run when the furnace was in good operating condition, for a new lining had been put in the day previous to the first test.

The door heat-loss measurement was by far the most difficult, owing to the necessity of handling the hot flues and fitting them tightly over the door openings. Several factors combine to vary the amounts of gas escaping through the different doors. Chief among these is the direction of the air currents through the foundry. Thus, during the latter part of the run a noticeable draft was blowing toward the right-hand charging door (No. 2) so the volume of gas escaping through this door was reduced while a corresponding increase was produced in the volume escaping from the tap hole (No. 3) and especially in the volume escaping from the left-hand charging door (No. 1). These changes are clearly shown by the gas volumes issuing from the different doors.

Each time flux was added to the bath the gas volume was appreciably increased for several minutes while flames shot out through the door openings. Just after the furnace is charged the gas volume is greater, due to the driving off of moisture and other volatile constituents of the charge and to the combustion of oil on the scrap steel. This probably accounts for the high heat loss through the doors at the beginning of the run.

As shown by the tables the loss increased toward the end of the run, being a maximum at tapping time. This is perfectly natural, for it is at that time that the furnace temperature is a maximum.

There is comparatively little gas generated in the simple melting-down operation. It was observed that a considerable portion of the furnace gases must be supplied by cold air flowing in under the charging doors through the opening between door and sill, where an appreciable in-draft was noticed. The furnace thus has to heat up this unnecessary air and then discharge it at a high temperature through the openings at the top of the charging doors and tap hole. This means lower efficiency.

The charging-door loss could be reduced very materially by making the doors fit closely against the furnace walls so as to cut off as much as possible the air flowing in at the bottom and the outgoing gases through the opening at the top. In the design of subsequent furnaces of this type two methods could be employed to accomplish this result:

First: By the use of a round charging door in the form of a plug mounted to swing on vertical trunnions. This does away with counter weights and permits the door being made thick enough to reduce leakage to a small amount.

Second: By having the furnace walls slightly inclined inward at the charging door ends and using vertically sliding doors with counter balance. The pull of gravity would then hold the doors with sufficient firmness against the walls.

The electrode heat loss is a necessary evil. Of course, the more electrodes through the roof the greater this loss amounts to, so the only way to minimize this loss on a small furnace is to run on single phase. Graphite electrodes were used on this furnace, which means a higher heat loss than with amorphous carbon electrodes.

The high electrode loss at the beginning was due to the fact that the electrodes, which were very hot from the previous heat, had been raised up to allow for the new charge, so that the surface ordinarily well below the water jackets was exposed and the portion next to the water jackets was red hot. This made the surface temperatures at first higher than they would be if the furnace was started cold. As the furnace temperature rose toward the end, the electrode loss naturally rose. This rise was more noticeable in the heat carried off by the cooling water than in that traveling up the electrode by conduction. The temperature at the two marks on each electrode did not change as much as might be expected, because the electrodes, after being pushed a maximum distance down into the bath when the charge was first melted down, were gradually withdrawn, so that the marks rose higher and higher above the water jackets. If the furnace temperature had remained constant, the surface temperature at the marks would have fallen.

The formulas used in calculating the heat passing out through the electrodes depend on the assumption that the electrodes have uniform cross section throughout their length, that the conductivities for heat and electricity are linear functions of the temperature, and neglect the loss by radiation from the electrode surface between the points at which the temperatures were taken. Since the distance between these points was comparatively small this radiation loss amounted to very little. The electrodes were uniform in cross section throughout.

The heat carried off in the water from the electrode water-jackets is not all from the electrodes, but a considerable part is from that part of the roof adjacent to the electrode openings. However, this loss is made necessary by the electrodes and so may be counted under the head of electrode losses.

CONCLUSION.

By integrating the door and electrode loss curves and dividing these areas by their length, the average door and tap hole loss was found to be 12.5 per cent and the electrode loss 7.3 per cent of the power input to the furnace. The electrode loss can not be cut down much so long as graphite electrodes are used, but the door loss can be reduced a considerable amount by making the charging doors fit closely against the furnace walls, and the tap hole loss reduced by suitable closing devices.

The commission in charge of the Chilean Government loans to nitrate producers in Chile, organized under Government decrees of August 13 and 18, 1914, has reported to the Minister of Finance that the operation of the law providing for such Government loans reached its maximum activity between August and December of 1914. Since that time the tendency has been toward a balancing of these obligations on the part of the nitrate producers as a result of the increasing sale of nitrate. Up to July 31, 1915, the loans totaled $863,464, the liquidations, $722,949, and the interest collected, $89,351. The net expenses to the Government in the operation of these loans from August, 1914, to July 31, 1915—which expenses include the salaries of a cashier and secretary for this department—were $3,287.

A recognized organ of the grain trade, the London Grain, Seed, and Oil Reporter, estimates that the world's wheat crop in the present year will reach the total of 518,500,000 quarters (quarter equals 480 pounds), as compared with 456,500,000 quarters in 1914 and 494,650,000 quarters in 1913. The indicated surpluses in exporting countries, judging from present crop conditions, work out at the figure of 132,500,000 quarters, leaving reserves at the end of the season of the same total as at the commencement. This figure is arrived at as follows: Russia and Roumania, 40,000,000 quarters; United States, 45,500,000 quarters; Argentina, 13,000,000 quarters; Canada, 18,000,000 quarters; India, 8,000,000 quarters; Australia, 7,000,000 quarters; and North Africa, 1,000,000 quarters.

THE LABORATORY

USE OF THE FLAME ARC IN PAINT AND DYE TESTING.*

By WM. ROY MOTT.

INTRODUCTION.

The white-flame arc at 25 amperes affords light at two feet (60 cm.) distance more intense than summer sunlight; and unlike sunlight, this white light is exactly reproducible and available twenty-four hours in every day. Sunlight varies continually, due to shifting solar position and changing atmospheric conditions. Dyes and paints have been generally tested in sunlight because until the invention of the high amperage white-flame arc, sunlight was the most intense light practically available. Some good work has been done with the pure carbon arc (Ref. 3, 23) and with the quartz mercury arc (Ref. 23, 24, 60); but these are limited in value, the first by low intensity and the second by the source of the action being ultraviolet light, which is often different from the action of ordinary light. The high amperage white-flame arc has forced out all other forms of illumination as the cheapest, most powerful light source for photo-engraving. It is taking its legitimate place for blue-printing, for photographic studio work, and for laboratory and industrial manufacture of chemicals by light. The writer has made several hundred comparisons of the action of sunlight and of white-flame arc light on dyed fabrics and on paints and feels that sufficient has been done to invite a general consideration of this light in dye and paint investigations. There are great possibilities of new apparatus, of new fields and of a re-survey of the general field under definite, reproducible and efficient conditions. A brief summary of the literature given at the end of this paper shows much that needs to be investigated under conditions so arranged that anyone can repeat the experiments.

GENERAL FACTORS.

The action of light on dyes may take the following courses: (1) Fading without other color change, (2) Darkening before fading, (3) change to a different color tint, and (4) composite effect as to depth into cloth, so that on viewing underhand (overhead) the cloth is darkened and on viewing overhand (at an angle) the cloth appears faded. The fastness of dyes may run through extremes of fading in a few hours in sunlight to lasting several months. Graded steps of exposure are necessary to follow the results, which are often complex combinations. There are six major factors affecting the action of light. These are: (1) kind and intensity of light, (2) atmosphere, (3) dye, (4) fiber, (5) mode of applying dye, including mordants, fillers, etc., and in paints, nature of oil and varnish medium, (6) temperature. In the summary of the literature, several references to each of these factors are to be found.

(1) *Kind and Intensity of Light:* (Ref. 2, 4, 49). The light has the least action when of the same color as the dye, due to the first law of conservation of energy, that the energy reflected cannot do chemical work. The complementary color (light absorbed), as pointed out by Bancroft and others, has the most action. In case of absorption of blue and other rays (red or green) there is generally more effect with the blue rays than with red or green. The effect of intensity of light is such in some cases as to entirely change the reaction. Even in simple cases the curve changes through three or four types of equations. The intermediate step generally obeys a logarithmic law for photographic paper. At very low intensities there seems to be a limiting point of reaction. Also, in some cases there is a storage of energy so as to obtain effects similar to latent images. (Ref. 8, 22.)

(2) *Atmosphere:* (Ref. 1, 12, 15, 16, 39, 41). By working in vacuum many fugitive dyes resist sunlight. There are a few rare exceptions. Gebhard says that under every-day conditions oxidation is the chief factor. The protective action of varnishes is, according to Toch, to prevent oxidation. Moisture in the air is favorable to the immediate action of light. Vapors of ammonia or alcohol greatly increase the action of light. Highly diluted acids, as found near towns, act protectively.

(3) *Dyes:* The constitution of the dyes has been studied in relation to fading by Gebhard and many others. Many of the coal-tar dyes are reported as fast as the best mineral pigments.

(4) *Fiber:* Many dyes have similar effects on silks and wools. With cottons, there are greater differences. On paper, it is very difficult to get a fast dye. (Ref. 35, 42.)

(5) *Mode of Applying Dye, Including Mordants, Filters, etc.*, and, in paints, nature of oil and varnish medium. The references cover details too complex to give here. (Ref. 9, 31, 36, 39, 44, 45, 52.)

(6) *Temperature:* In general, the temperature coefficients of light reactions are small. I have, however, discovered exceptional results with lithophone, but even here the results are probably due to the super-

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position of secondary chemical actions. (Ref. 28, 29, 57, 67.)

TESTING IN SUNLIGHT.

Tests have shown that the chemical action of sunlight often varies to double in power, although the sky may be clear. The sunlight varies because of variations in solar emission, shifting position of sun, and changing atmospheric conditions. Noon sunlight is usually several times stronger in action than four hours sooner or later. In the winter time the actinic values are several times lower than in the summer, and the day is only about half as long. Daylight means an expensive arrangement for protecting against rain, wind, etc. "One observer may expose his patterns in the open to the joint action of sunlight, wind, rain, and possibly frost; another may expose under glass and place the patterns so as to get the largest possible proportion of the direct rays of the sun, or he may perhaps expose in diffused daylight only.

"Again, the depth of the shade, the climate, the condition of the atmosphere, the time of the year, are all important factors which must necessarily be taken into account if anything like an accurate result is to be arrived at. With the possibility of such varying conditions, it will be easily understood how one observer may obtain a result which leads him to infer that a color is not fast, whereas another, who may have exposed the same color for the same length of time, concludes that the color is fast. It is to be regretted that we have no recognized standard for testing of color as to their fastness to light, and much credit would be due to anyone who would take the trouble to work this out. It would undoubtedly be a step in the right direction if, when exposing to direct sunlight under glass, we could agree as to which position the board, on which the patterns are fixed, should be placed in, and, in giving the result, mention the number of hours of direct sunlight (measured by the sun recorder) and of diffused light to which the patterns have been exposed. By a series of experiments, the ratio of destructive action of direct sunlight and the average of diffused daylight could possibly be determined, and we should thus be enabled to express the duration of exposure in one term, *viz.*, hours of direct sunlight. If this were done, there would be much less divergency of opinion regarding the fastness of colors to light. For exact measure, however, it would be necessary to measure the average intensity of the sun's rays during the different seasons of the year and for different climates." (See Knecht, Rawson and Loewenthal, page 744.) The method of testing used by these gentlemen was to expose under glass, facing south, with part of the pattern covered with thick cardboard. "If it has stood a month's exposure in summer without any material alteration, it may be called fast."

My sunlight tests were made in June, without glass, under direct sunlight in the hours 7:30 a. m. and 4:45 p. m. The patterns were placed horizontally. The patterns were taken indoors whenever the sun was obscured by clouds. Fifty hours of such direct sunlight required between two and three weeks. The exposure was on the roof of a building receiving light from nearly all the sky as well as from the sun. I find that the actinic power of the blue sky varies between 20 and 50 percent of the total effect. By measuring the actinic effect of a ray of sunbeam let into a dark room, the light of the sky is largely eliminated. If the sky is overcast with clouds then the diffused light may become nearly 100 percent of the total.

In the literature (Ref. 5, 30, 32, 44, 51) summarized at the end of this article, it will be found that considerable work has been done to measure the changing actinic effect of sunlight, but a complete solution has not been secured. Gebhard (Ref. 33) points out that sunlight is variable in color as well as amount. The devices proposed for measuring chemical action of sunlight are clumsy, but it must be admitted are better than no effect at standardization. Probably the standardized results afford a variation of 20 percent. The unstandardized results are often such that the stronger effect may be twice the weaker.

THE 5,000 M. S. C. P. WHITE-FLAME ARC.

The high amperage white-flame arc has been in use only a few years, but practically all photo-engravers have adopted it because of its efficiency, power and quality of light, which is the best known for color-process work.

The outside spectrum is that of the white-flame arc, which is seen to have an enormous number of light-giving lines filling the spaces between the cyanogen bands and superposed upon them, resulting in a better light than the enclosed arc even at the same or greater efficiency. The spectrum of the white-flame arc is *equally* rich in the green, yellow and red regions. The extreme closeness of the lines gives a light nearly the same in continuity as sunlight, which has its dark lines (Fraunhofer lines). The candle power of the high amperage white-flame arc is exceptional in tremendous size of unit available and of greater efficiency than other forms of illumination. The following table contains average results as to mean spherical candle power and mean spherical photographic power. The average relative time to affect equally folio paper with the lights in a two-meter sphere is the basis of photographic power. We can all admit, as Mees says, that this is no scientific definition. A 28-ampere Aristo lamp was used with white flame carbons under open arc conditions and without any globe. A comparison with the nitrogen-filled lamp is given:

TABLE I.

	Line Volts.	Arc Volts.	Amperes.	Mean Spherical Candle Power.	Mean Spherical Photo. Power.
White-Flame Arc (open)	115	63	28.	5130	100
Nitrogen lamp—clear globe	117	117	6.7	866	4
Nitrogen lamp—blue globe	115	115	8.5	485	5

It is extremely conservative to say that for an equal amount of electrical energy the photographic power of the white-flame arc is six to ten times greater than that of the nitrogen filled incandescent lamp.

GENERAL NOTES ON LAMPS AVAILABLE.

The above tests were made with the Aristo lamp on direct current. Tests with alternating current show greater value, due to the response of the flame arc to the voltage component of the power and to other factors. The photographic power of the flame arc increases nearly four times when the current is doubled and nearly proportional to the arc voltage. On a fluctuating line voltage it varies less than half as much as the nitrogen-filled incandescent lamp and is perfectly indifferent to all kinds of electrical and mechanical shocks. There is thus a greater service power for reproducing results. In most of these tests an Aristo lamp was used on 110 volts with the globe removed. An ordinary 5 ampere, enclosed arc lamp can be arranged with a shunt to carry 20 amperes at 55 volts around the lamp resistance and solenoid, to operate at 55 amperes at the flame arc. A publication of this arrangement will be made in detail later.

There are a large number of standard lamps on the market that can be adopted. The Macbeth, Bogue and Helios are commercial lamps used in photo-engraving. In some of the fading tests, a 220 volt Macbeth flame arc at 25 amperes and 90 arc volts was used.

LIGHT OF DIFFERENT FLAME CARBONS.

The most valuable flame carbon for fading tests is the snow-white flame carbon. This has the maximum actinic power with or without the interposition of glass. Also it approaches very closely to sunlight with blue skylight. The flame carbons were used chiefly in 10 mm. x 305 mm. as lower positives with an ordinary ½ x 12-inch (1.3 x 30 cm.) enclosed arc cored upper carbon. In some cases ½ x 12-inch (1.3 x 30 cm.) flame cored carbons were used. The chief characteristics of these carbons are given in the following table:

TABLE II.

	Light.	Photo. Power.
Snow-white flame carbon.	Like sunlight plus blue skylight.	100
"Blue" flame carbon......	Rich in ultraviolet.............	60
Yellow flame carbon.....	Rich in red, yellow and green.	35
Red flame carbon	Rich in red.....................	30
Pure carbon arc, (10 mm. shell)........	Next to snow-white in quality.	40

The photographic power represents the inverse of average time to attain equal shades with solio paper. The effect here is chiefly that of the short waves.

TEST ARRANGEMENTS.

The best arrangement so far has been with a set of 20-inch (50 cm.) hoops around the Aristo lamp at 28 amperes. This provided a good circulation of air to keep the samples cool and for carrying the arc products up. There were tested at the same time a couple of hundred of small samples secured from standard dye houses. Only a small piece of sample was exposed and the rest covered with heavy blotting paper. Then the other end of these same samples was exposed to sunlight for fifty actual hours of sunshine. Also tests were made in front of a 25 ampere, 220 volt Macbeth lamp with 90 arc volts. In this case, a flat board was used and no correction for the change in distance from the light was possible. No doubt, much better arrangements can be developed.

COMPARISON OF ACTION OF SUNLIGHT AND WHITE-FLAME ARC.

A sample book entitled, "The 1912, Fashionable Colors," was obtained from Farbwerke vorm. Meister Lucius and Brüning, Hoechst am Main. This gave the following results for the standard color on wool. (The goods are dyed 1½ hours at the boil in an acid bath with addition of 10 to 20 lb. Glauber's salt and 3 to 5 lb. sulphuric acid or with 7½ to 12½ lb. tartar substitute. The amounts refer to 100 pounds of material.)

Per cent.	Dye.	Standard Colors. Exposed to 50 Hours June Sunlight.
2	Flavazine L	No change.
2	Flavazine S	No change.
2	Flavazine T	No change.
2	Victoria Scarlet 2R.....	No change.
3	Brilliant Crimson O.....	No change.
2	Sulpho Rosazeine B.....	Darkens with loss of brightness.
1½	Amido Naphthol Red BB.	No change.
1½	Amido Naphthol Red 6B.	No change.
3	Alizarine Direct Blue E_3BO	Darkens with loss of brightness.
1½	Patent Pure Blue O.....	Darkens with loss of brightness.
2	Patent Blue V new	Darkens with loss of brightness.
3	Naphthalene Green V...	Darkens with loss of brightness.
2	Acid Violet 6BN	Slight change.
3	Amido Blue GGR.......	No change.

Viewing at an angle, the fading is of course lighter. The five dyes showing most effect alone are equally conspicuous in the mixtures. As the dye is diluted with unlike color, the effect becomes sharper. The effects in sunlight for 50 hours were duplicated by the light of the white flame in 10 to 20 hours. This was also true of the 132 mixtures. The fading action was far more marked with dilute solution. For example 1/16 percent Sulpho Rosazeine B was nearly bleached, although 2 percent showed only a slight darkened effect viewed directly from above. The action of light on Sulpho Rosazeine B was marked in mixtures, 25, 26, 27, 67, 68, 69, 73, 74, 75. These numbers refer to the 1912 book. The Patent Blue V new showed marked change in 10, 11, 12, 13, 14, 15, 127, 128, 129 The Patent Pure Blue O changed much in 67, 68, 69. The Alizarine Direct Blue showed marked changes in 4, 5, 6, 7, 8, 9, 13, 14, 15, 34, 35, 36, 49, 50, 51, 52, 53, 54. Dyes with Naphthalene Green V showed only slight changes. The most marked color change was with 127, 128 and 129. Here a bright blue changed to a reddish purple. No. 127 consisted of 0.6 percent Sulpho Rosazeine B, 0.15 percent Patent Blue V new, 0.02 percent Alizarine Direct Blue. All these colors separately are affected by light and hence the unusual effect on the composite is not surprising.

The 1914 Color Book of the Farbwerke vorm. Meister Lucius & Brüning, Hoechst am Main, shows a marked improvement in the fastness to light of the dyes of the 1912 book. None of the color mixtures

	50 HOURS SUNLIGHT.		100 HOURS FLAME ARC.	
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Fast Acid Yellow 3G	No change	No change	Slightly darker	Slightly darker
Fast Acid Yellow TL	" "	" "	" "	" "
Naphthol Yellow S	Faded	Darkened	Much faded	Much darker
Acid Yellow AT	No change	No change	No change	No change
Milling Yellow G pat	" "	" "	" "	" "
Milling Yellow O pat	" "	" "	Faded	Darker
Fast Yellow S	" "	" "	"	"
Metanil Yellow	Slight	Slight	"	"
Indian Yellow FF	Darkened	Darkened	Much darker	Much darker
Indian Yellow R	"	"	" "	" "
Indian Yellow G	Much darkened	Much darkened	" "	" "
Tropaeoline G	Slightly faded	Darkened	Faded	" "
Tropaeoline OO	" "	"	"	" "
Orange IV	" "	"	"	" "
Orange GG	No change	No change	Slightly faded	No change
Orange EN	" "	" "	" "	" "
Orange II	" "	" "	No change	" "
	1 PER CENT.	2 PER CENT.	1 PER CENT.	2 PER CENT.
Orange Extra	No change	No change	Slightly faded	No change
Orange R	" "	" "	" "	" "
Orange ENZ	" "	" "	" "	" "
	2 PER CENT.	4 PER CENT.	2 PER CENT.	4 PER CENT.
Scarlet FR	No change	No change	Slightly faded	No change
Scarlet FRR	" "	" "	" "	" "
Scarlet FRRR	" "	" "	" "	" "
Brilliant Scarlet GG	" "	" "	" "	" "
Brilliant Scarlet G	" "	" "	" "	" "
Brilliant Scarlet R	" "	" "	Faded	" "
Brilliant Scarlet RR	" "	" "	"	Slightly faded
Brilliant Scarlet 3R	" "	" "	"	" "
Brilliant Scarlet 4R	" "	" "	"	Faded
Brilliant Scarlet 6R	" "	" "	"	"
Crystal Scarlet 6R	" "	" "	Slightly faded	No change
Brilliant Cochineal 2R	" "	" "	" "	" "
Brilliant Cochineal 4R	" "	" "	" "	" "
Brilliant Croceine B	" "	" "	" "	" "
Brilliant Croceine M	" "	" "	Faded	" "
	2 PER CENT.	4 PER CENT.	2 PER CENT.	4 PER CENT.
Brilliant Croceine MOO	No change	No change	Faded	No change
Brilliant Croceine 3B	" "	" "	"	" "
Brilliant Croceine 5B	" "	" "	"	" "
Brilliant Croceine 9B	" "	" "	"	" "
Croceine AZ	" "	" "	"	" "
Azo Rubine	Slight fading	Very slight	"	" "
Roccelline	" "	" "	"	" "
Naphthol Red EB	" "	" "	"	" "
Naphthol Red C	" "	" "	"	Slightly faded
Amaranth	" "	" "	"	No change
Azo Red A	" "	" "	Much faded	Faded
Amaranth B	No change	No change	Slightly faded	No change
Wool Red B	" "	" "	" "	" "
Milling Red FR	" "	" "	" "	" "
Milling Red G	" "	" "	" "	" "
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Lanafuchsine SG	Slight fading	Very slight	Faded	Slightly faded
Lanafuchsine SB	" "	" "	"	Faded
Lanafuchsine BBS	" "	" "	Much faded	"
Brilliant Lanafuchsine GG	" "	" "	" "	No change
Brilliant Lanafuchsine SL	" "	" "	" "	" "
Brilliant Lanafuchsine BB	" "	" "	" "	" "
Azo Orseille BB	" "	" "	" "	" "
Lanafuchsine 6B	" "	" "	" "	" "
Acid Magenta	" "	" "	" "	Darker
Archil Substitute N powder	Faded	Slight fading	" "	Slightly faded
Acid Violet 4RS	"	" "	" "	Faded
Azo Wool Violet 7R	Slight fading	Very slight	" "	Slightly faded
Alkaline Violet CA	Faded	Darkened	" "	Faded
Formyl Violet 4BF	"	"	" "	"
Formyl Violet S4B	"	"	" "	"
Formyl Violet S5B	"	"	" "	"
	50 HOURS SUNLIGHT.		100 HOURS FLAME ARC.	
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Formyl Violet 6B	Faded	Darkened	Much faded	Faded
Formyl Violet 10B	"	"	" "	"
Acid Violet 6BS	"	"	" "	"
Acid Violet 6BC	"	"	" "	"
	3 PER CENT.	5 PER CENT.	3 PER CENT.	5 PER CENT.
Azo Fast Violet 2R	No change	No change	Slightly faded	No change
Azo Wool Violet 4B	" "	" "	Faded	Slightly faded
Azo Fast Blue B pat	Slight	" "	"	" "
Azo Fast Blue BD pat	No change	" "	"	" "
Azo Fast Blue BR conc. pat	" "	" "	"	" "
Azo Wool Blue 6B pat.	Slight	" "	Much faded	Faded
Azo Wool Blue SE pat	"	" "	" "	"
Azo Wool Blue B pat	"	" "	" "	"

	50 HOURS SUNLIGHT.		100 HOURS FLAME ARC.	
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Azo Wool Blue SER pat	“	“ “	“ “	“
Azo Wool Blue C pat	No change	“ “	“ “*	“*
Azo Navy Blue 3B pat	Slight	“ “	Faded	“
Azo Navy Blue B pat	“	“ “	“	“
Brilliant Naphthol Blue 4B pat	“	“ “	“	“
Brilliant Naphthol Blue B pat	“	“ “	“	“
Brilliant Naphthol Blue R pat	“	“ “	“	“
Acid Navy Blue A pat	“	“ “	“	“
Fast Navy Blue G pat	No change	“ “	Slightly faded	Slightly faded
Fast Navy Blue B pat	“ “	“ “	“ “	“ “
Azo Merino Blue G pat	“ “	“ “	“ “	“ “
*Reddish tint at end.				
	3 PER CENT.	5 PER CENT.	3 PER CENT.	5 PER CENT.
Azo Merino Blue 3B pat	No change	No change	Slightly faded	Slightly faded
Peri Wool Blue G pat	“ “	“ “	No change	No change
Peri Wool Blue B pat	“ “	“ “	“ “	“ “
Lanacyl Blue BB pat	“ “	“ “	“ “	“ “
Lanacyl Blue BN	“ “	“ “	“ “	“ “
Lanacyl Blue R pat	“ “	“ “	“ “	“ “
Lanacyl Blue RN	“ “	“ “	“ “	“ “
Lanacyl Navy Blue BB pat	“ “	“ “	“ “	“ “
Lanacyl Navy Blue B pat	“ “	“ “	“ “	“ “
Lanacyl Violet BF pat	“ “	“ “	“ “	“ “
Naphthol Blue G	“ “	“ “	“ “	“ “
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Cyanole FF	Faded	Darkened	Much faded	Faded
Cyanole extra	“	“	“ “	“
Cyanole extra H	“	“	“ “	“
Cyanole AB	“	“	“ “	“
Tetra Cyanole extra	“	“	“ “	“
Tetra Cyanole SF	“	“	“ “	“
Tetra Cyanole V	“	“	“ “	“
Tetra Cyanole A	“	“	“ “	“
Thiocarmine R powder	“	“	“ “	“
Cyanole Navy Blue KR	“	“	“ “	“
Indigo Blue N	Very faded	Faded	“ “	“
Indigo Blue SGN	“ “	“	“ “	“
Formyl Blue B	“ “	Darkened	“ “	“
Brilliant Milling Blue B	“ “	“	“ “	“
Alizarine Cyanole EF pat	Faded	No change	“ “	“
Alizarine Cyanole SR pat	“	“ “	“ “	“
Alizarine Cyanole SB pat	“	“ “	“ “	“
Alizarine Cyanole SG pat	“	Slight change	“ “	“
Alizarine Cyanole Violet R pat	“	No change	Faded	Darker
	0.5 PER CENT.	1.5 PER CENT.	0.5 PER CENT.	1.5 PER CENT.
Alkaline Blue 6B	Faded	Slight fading	Much faded	Faded
Alkaline Blue 4B	“	“ “	“ “	“
Alkaline Blue 3B	“	“ “	“ “	“
	0.9 PER CENT.	2.3 PER CENT.	0.9 PER CENT.	2.3 PER CENT.
Alkaline Blue 2R	Faded	Slight fading	Much faded	Faded
	0.5 PER CENT.	1.5 PER CENT.	0.5 PER CENT.	1.5 PER CENT.
Pure Soluble Blue	Faded	Very slight	Much faded	Faded
Water Blue B	“	Darkened	“ “	“
Water Blue RB	“	No change	“ “	“
Water Blue R	“	“ “	“ “	“
	50 HOURS SUNLIGHT.		100 HOURS FLAME ARC.	
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Blue RS	Faded	No change	Much faded	Faded
	0.5 PER CENT.	1.5 PER CENT.	0.5 PER CENT.	1.5 PER CENT.
Wool Blue TB	Faded	No change	Much faded	Faded
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Acid Green 5C	Faded	Faded	Much faded	Faded
Acid Green extra conc.	“	Darkened	“ “	“
Acid Green extra conc. B	“	“	“ “	“
Cyanole Fast Green G pat	“	“	“ “	Darker
Brilliant Milling Green B	“	“	“ “	Faded
Fast Acid Green BN	“	“	“ “	“
Cyanole Green 6G	“	“	“ “	Darker
Cyanole Green S	“	“	“ “	“
Cyanole Green B	Slightly faded	“	“ “	“
Alizarine Brilliant Green G pat	No change	No change	Slightly faded	No change
	2 PER CENT.	6 PER CENT.	2 PER CENT.	6 PER CENT.
Naphthol Green B	No change	No change	Faded	Darkened
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Naphthol Dark Green G	Slight fading	No change	Much faded	Faded
	4 PER CENT.	7 PER CENT.	4 PER CENT.	7 PER CENT.
Naphthol Black 6B	No change	No change	No change	No change
Naphthol Black 3B	“ “	“ “	“ “	“ “
Naphthol Black SG	“ “	“ “	“ “	“ “
Naphthol Black B	“ “	“ “	“ “	“ “
Naphthol Black P	“ “	“ “	“ “	“ “
Naphthol Blue Black SB	“ “	“ “	“ “	“ “
	3 PER CENT.	5 PER CENT.	3 PER CENT.	5 PER CENT.
Naphthol Blue Black S	No change	No change	No change	No change
Naphthol Blue Black	“ “	“ “	“ “	“ “

Some thirty other blacks showed no change.

	50 HOURS SUNLIGHT.		100 HOURS FLAME ARC.	
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
	0.5 PER CENT.	1.5 PER CENT.	0.5 PER CENT.	1.5 PER CENT.
Silver Grey N	Faded	Faded	Much faded	Much faded
Nigrosine soluble in water	"	"	" "	" "
Aniline Grey B	"	"	" "	" "
Induline B	"	"	" "	" "
	2 PER CENT.	4 PER CENT.	2 PER CENT.	4 PER CENT.
Solid Blue R	Very slight	No change	Slightly faded	Darker
Solid Blue 3R	No change	" "	" "	No change
	3 PER CENT.	5 PER CENT.	3 PER CENT.	5 PER CENT.
Gloria Black B	No change	No change	No change	No change
Neutral Wool Black 4B	" "	" "	" "	" "
Neutral Wool Black B	" "	" "	" "	" "
Azo Wool Black G	" "	" "	" "	" "
	0.5 PER CENT.	1.5 PER CENT.	0.5 PER CENT.	1.5 PER CENT.
Eosine 3G	Faded	Darkened	Much faded	Much faded
Eosine GGF	"	"	" "	" "
Eosine BN	"	"	" "	" "
Erythrosine B	"	Faded	" "	" "
Erythrosine extra N	"	"	" "	" "
	1 PER CENT.	3 PER CENT.	1 PER CENT.	3 PER CENT.
Phloxine S	Faded	Darkened	Much faded	Much faded
	0.5 PER CENT.	1.5 PER CENT.	0.5 PER CENT.	1.5 PER CENT.
Phloxine	Faded	Darkened	Much faded	Much faded
Rose Bengale extra N	"	"	" "	" "
Rosazeine B	Slightly faded	No change	Faded	Faded
	0.1 PER CENT.	0.3 PER CENT.	0.1 PER CENT.	0.3 PER CENT.
Rosazeine B extra	Very slight	No change	Faded	Faded

faded nearly as much as those of 1912. In these tests 50 hours of sunlight was compared with 25 hours of the light of a 220 V. 25 A. Macbeth white-flame arc at two feet distance. The flame arc light had the same kind of an effect as sunlight. With the blues and greens, there was fading as before, and no change occurred with 2 percent yellows or reds. The troublesome Sulpho Rosazeine B (of 1912) was eliminated. A new brown (Amido Yellow E, pat.) had been added. This darkened a little.

The Amido Naphthol Red BB at 0.6 percent showed a little fading. A mixture (No. 125) of 0.6 percent Amido Yellow E. 0.06 percent Alizarine Direct Cyanine 3 G and 0.009 percent Patent Blue V new, showed a change from olive green to a decided brown. The Naphthol Green V and Patent Blue V new showed the most change under light.

Cassella Color Company—Catalogue No. 3317, Dyestuffs for Wool, gave the following results, comparing 50 hours sunlight and 20 hours light of white-flame arc at 10 inches (25 cm.), with good ventilation. The white flame arc gave nearly the same effect as sunlight, for this reason a separate column is not given for 100 hours with the flame arc, equivalent to about a year of ordinary light.

A series of ninety chromated dyes showed no change in 50 hours of sunlight or in the light of white flame arc for 20 hours.

A series of sixty diamine dyes showed a few fading of blue in sunlight. The tests in the flame arc light were not completed, but the action was in same direction as far as tested.

Some aniline colors from The Heller and Merz Company gave the following results:

On Wool.	50 Hrs. Sunlight.	10-20 hrs. Flame Arc, 10 in. (25 cm.)
Patent Blue B	Darkened	Darkened
Acid Violet 4BNS	Darkened	Darkened
Acid Green 2CX	Darkened	Darkened
Naphthol Yellow L	Darkened	Darkened
Chrysophenine E. S. Conc.	Slight darkening	Slight darkening
Scarlet 4R Brilliant	No change	No change

These also resisted distilled water except the blue The yellow and blue were most affected by light.

On Cotton	50 Hrs. Sunlight.	10-20 hrs. Flame Arc, 10 in. (25 cm.)
Pheno Blue 7B Conc.	Darkened	Darkened
Pheno Violet BK Conc.	Slightly darkened	Slightly darkened
Pheno Green KDX	Slight change	Slight change
Primuline Conc.	Much darkened	Much darkened
Chrysophenine E. S. Conc.	Slight change	Slight change
Pheno Orange R	Darkened	Darkened
Pheno Fast Scarlet 4B	Darkened	Darkened

All these cotton dyes, except the light yellow, gave colored solutions with distilled water. In 6 hours' direct sunlight the yellow had darkened to a brownish yellow. The action of the white flame arc light was the same as sunlight. With cottons and the Macbeth 220 volt at two feet, some fading was obtained in two hours for Primuline conc., Pheno Violet 3K conc. and Chrysophenine E. S. conc.

Some cheap bunting (retailing at 5 cents a yard) was secured from a store in Cleveland. These were said by the merchant not to be fast to light.

Color.	50 Hrs. Sunlight.	8½ hrs. Macbeth Lamp, 2 ft. (60 cm.)
Black	No change	No change
Violet	Greatly faded	Faded
Dark Blue	Greatly faded	Slight fading
Baby Blue	Change to pure white	Bleached
Dark Green	Faded	No change
Light Green	Change to pure white	Nearly bleached
Yellow	Greatly faded	Nearly bleached
Red	Turned brown	No change
Purple	Greatly faded	Nearly bleached

The four most rapidly fading buntings were made the basis of several comparisons as to effect of increasing increments by 1 hour of exposure, of effect of light from different flame carbons, of light from different flame lamps and of comparison of D. C. and A. C.

Tests on bunting, using an Aristo 28 ampere, 110 volt lamp with white flame carbons and using hoop of

20 inch (50 cm.) diameter. Exposures were in steps of one hour increments. The significant data are:

inches (25 cm.). The 10 hours of the white flame arc gave in all cases more effect than 60 hours of sunlight.

	1st Hour.	2d Hour.	4th Hour.	10th Hour.
Baby Blue	Slightly faded	Faded	Bleached	Bleached
Pink	Faded	Much faded	Bleached	Bleached
Purple	Slightly faded	Faded	Nearly bleached	Bleached
Light Green	Very slight	Slight fading	Faded	Much faded

	Corresponding time with Aristo at 10 Inches (25 cm.).			
Light Used.	Baby Blue.	Pink.	Purple.	Light Green.
220 V., 25 A., White flame arc at 2 ft.	1 hour	1 hour	1 hour	1 hour
220 V., 25 A., "Blue" flame arc	2 hours	3 hours	5 hours	2 hours
220 V., 25 A., Yellow flame arc	1 hour	1 hour	1 hour	No change
220 V., 25 A., Red flame arc	No change	No change	No change	No change
220 V., 25 A., Pure carbon arc	2 hours	3 hours	5 hours	2 hours

These now afford a basis for measuring time of fading to equal extent by other forms of illumination.

The "Blue" flame arc was very rich in ultraviolet light and had over twice the effect on the purple as on the baby blue or light green. It is unfortunate from the standpoint of dye fading that ultraviolet light often has very different proportional results on different dyes as compared with sunlight. With only two hours' exposure, the other buntings except the yellow showed practically no change. The light green and purple were faded a little more with sunlight at 50 hours than the Aristo at 10 inches (25 cm.) for 10 hours. The brightest June sunlight and skylight for 50 hours was more effective than 10 hours with Aristo at 10 inches (25 cm.) and less effective than 20 hours. The Aristo at 10 inches (25 cm.) was twice as powerful as the 220 volt Macbeth at two feet (60 cm.).

Comparison with a nitrogen filled lamp on 110 volts D. C. at 6½ amp. 1,000 watt unit with clear glass.

Table showing time for equal effect Aristo at 10 inches (25 cm.) with nitrogen, lamp at 10 inches (25 cm.) for one hundred hours:

	Time of Equal Effect Aristo.	Times Greater Speed with Flame Arc.
Baby Blue	3 hrs.	33
Pink	1 hr.	100
Purple	3 hrs.	33
Light Green	6 hrs.	17

The action of the incandescent light on the other bunting was as follows:

Black	No effect
Violet	Faded
Deep Blue	Faded
Green	Faded (more blue tone)
Yellow	Slightly faded
Red	No effect

The large excess of red and yellow rays and deficiency of blue rays has increased the action on the green (yellow absorbed) and decreased the action markedly on the red and yellow. The colors most easily faded by the incandescent lamp are the green and least easily faded are the reds and yellows.

Some comparisons were made between the D. C. Aristo and A. C. Aristo with a material advantage for the A. C. in speed.

Tests on linens. A little over one hundred samples of colored linens were exposed on separate parts to 50 hours' sunlight and 10 hours' white flame arc at 10 inches (25 cm.). This 50-hour period was not at the same time as the first set with the wools and cottons. The sky was somewhat murky and at times there were some small fleeting clouds during two of the days of the test. All the samples faded by sunlight were faded to a greater degree by the light of the white flame arc. Excepting black, none of the samples of dyed linen could resist 10 hours with the white flame arc.

ACTION OF PAINTS, WITH SPECIAL REFERENCE TO LITHOPHONE.

A number of sample books of the National Lead Company and Sherwin-Williams Paint Company were exposed to sunlight and to the light of the white flame arc and the similarity of action was noted. Samples supposed to contain chrome yellow turned green, perhaps by a reducing action of organic matter on the chromate. In many cases the tints were brightened by the bleaching of the linseed oil, etc.

Some tests by Mr. B. Perris, of the National Carbon Company, showed considerable fading of the best enamel sign paints after one hundred hours' exposure to light of a 25 ampere, white flame arc at 2 feet. This test is probably about equivalent to one year of ordinary sunshine in this latitude.

Lithophone ($ZnS.BaSO_4$) under the action of the light did not respond as rapidly as expected. Lithophone is well known to turn grey or even black on exposure to intense light, and later this dark color may turn to pure white in the absence of light or even in subdued light. Mr. O'Brien has published a very interesting article on the cause of the changes in color of lithophone. Two samples of lithophone were made up with a 1 percent solution of gum arabic and painted on glass with a camel's hair brush. This was allowed to dry and then it was exposed with the paint side to the light. The response was slight and mostly at the protected edges directly two feet (60 cm.) in front of the 220 volt Macbeth flame arc. I believed that the heat of the flame arc hastened the oxidation of the black zinc metal film as fast as formed and so I arranged the experiment with part of the plate cooled by being fastened by rubber bands on a large block (25 lb.-11 kg.) of ice. The part now kept cool by the ice blackened in a fraction of an hour and the part not cooled by the ice remained white after several hours. This experiment was conclusively repeated several times and proves the great importance of temperature as regards the blackening of lithophone under light. Under fifty hours of sunlight the lithophone darkened greatly. The interposition of glass greatly decreased the effect.

The following table shows that the maximum darkening of lithophone is given by the light of the "blue flame" arc due to its large amount of ultraviolet light. The tests were made at two feet (60 cm.) with 25 amps. arc at 90 arc volts on 220-volt D. C. line. Samples ice cooled.

	Exposure of ½ Hr.	On Standing in Dark.
White flame......	Blackened	White few hours
"Blue" flame	Rapidly blackened	Black after week
Yellow flame	Blackened	Black after week
Red flame	Blackened	White one hour

The parts not ice cooled remained white in all cases.

The blue flame arc gave the most effect. By exposing for five hours and keeping cool with ice, black coatings were obtained that were still black after one week. I have carefully read Mr. O'Brien's article and find no mention of this temperature effect, which appears to me to admirably support his theory of the cause of the blackening and subsequent whitening of lithophone. It also gives an added reason why lithophone is so well suited for interiors, with their higher temperatures.

J. CONCLUSIONS.

(1) For dye and paint testing as to fastness to light, there is found in the high amperage flame arc a light more powerful than sunlight, and, unlike sunlight, exactly reproducible.

(2) Different colored flame effects can be secured by using specially designed carbons which give colored lights as follows:

Snow-white flame carbons, nearly equal to sunlight plus blue sky.

"Blue" flame carbons, strong ultraviolet light.

Yellow flame carbons, rich in red, yellow and green but weak in blue. Some violet and ultraviolet.

Red flame carbons, strong in red light.

Pure carbon arc, far inferior to the snow-white flame arc.

(3) Hundreds of dyes have been compared in best June sunshine and in the light of the snow-white flame arc, with essentially similar results, but at much greater speed.

(4) The best June sunlight for 50 hours gave an effect equal to between 10 and 20 hours of 28 ampere white flame at 10 in. (25 cm.). A more definite statement is impossible owing to the large variations of sunlight on even clear days.

(5) The 1,000-watt nitrogen-filled incandescent lamp required 100 to 17 times greater exposure for equal effect at like distance than a 28-ampere flame arc with 55 volts at the arc. A deficiency in the blue in the light of the incandescent lamp caused considerably different results from sunlight.

(6) The "Blue Flame" arc was rich in ultraviolet light and therefore caused, with different dyes, results not proportional to sunlight.

(7) With the white flame arc tests could be made in 10 hours, requiring otherwise about two weeks with sunlight under the change of weather common in the northeastern part of the United States.

(8) Some cheap buntings (pink, baby blue, pale green) showed fading in one hour with the light of the white flame arc.

(9) Fading was most marked with diluted dyes. Same also shows in complex mixes.

(10) The 1914 colors showed marked improvements over the 1912 colors as regards fastness to light.

(11) Lithophone gave the maximum darkening (also of greatest persistency) by exposure to the light of the "blue flame carbons" rich in ultraviolet light.

(12) Experiments on lithophone showed maximum action at low temperatures. This result supports the theories of O'Brien and Bancroft on the cause of the darkening of lithophone. Also it gives an added reason why lithophone is especially suited for interior painting.

In conclusion, I hope that this work will prove a basis for many new investigations of both the practical and scientific aspects of the chemical action of light on dyes and paints. I here take pleasure in thanking those who have aided in this work. Dr. W. C. Moore, I thank for friendly aid; Mr. P. P. Bethea for care in experimentally following my directions, and I am under obligation to The National Carbon Co., whose facilities I enjoyed in doing this work. Also in the matter of samples, I have occasion to thank the firms Meister Lucins and Brüning, Heller and Merz, Cassella Color Co., Mott & Co., Sherwin-Willliams Paint Co., and others.

BRIEF SUMMARY OF LITERATURE.

The following are a few of the more important references. As this subject is as old as civilization, a complete bibliography would be out of question.

1. Jules Joffre: Bulletin de la Societé Chimique de Paris (3), I, May 5, 1889.

Chevreul (1837) showed that most dyes were not discharged in vacuum, but turmeric and prussian blue formed exceptions. Joffre found that most shades were unaffected in pure nitrogen, but those with picric acid were exceptions. The action of oxygen of air can also be eliminated by paraffin.

2. Depierre and Clouet: Jour. Soc. Dyers and Col., 1885, p. 245.

Seventy-six typical coloring matters on calico were examined in different colored light.

Strongest Action.	Least Action.	On Material Dyed
Yellow rays	Red rays	Red
Blue rays	Red rays	Orange, Yellow, Green
Yellow rays	Red rays	Blue
Blue rays	Red rays	Violet

3. Decoux: Jour. Soc. Dyers and Col. (1885), p. 247.

Electric arc light resembles sunlight in its action, but at 1.5 meters had one-fourth the effect of sunlight.

4. Dufton: Jour. Soc. Dyers and Col. (1885), p. 245.

Colors of light complementary to the dyed fabric act most rapidly. The dyed color is not appreciably affected by a light of the same color.

5. Dosne: Jour. Soc. Dyers and Col. (1901), p. 42.

Need of measuring the changing intensity of sunlight.

6. Brownlie: Jour. Soc. Dyers and Col. (1902), p. 295.

Ammonia, alcohol, or pyridine vapors enormously increase the action of light on dyes. Naphtha and chloroform slightly retard it.

7. Brit. Assoc. Reports, Section B, 1893, 1894, 1895, 1896 and 1898. See Chemical News, 64, 119; 68, 155, 170; 70, 154; 169, 74, 205, 218; 78, 175; 205, 215.

Several hundred commercial dyes of all colors at 2 per cent on various fibers were tested under glass against sunlight and daylight in sets, for 5, 10, 15, 35, and 55 weeks. Colors were divided in five classes as to fastness.

8. Weigert: Ann. Physik (1908), 24, 243-66.

Chemical action under light. "Active" condition after removal of light. Temperature coefficients of light reactions in general small.

9. Hoffman: Text. Farber Ztg. (1907), 6, 779.

Examination of colors in artificial light.

10. Toch: J. Soc. Chem. Ind. (1908), 37, 311.

Influence of sunlight on paints and varnishes. Glass is protective, red slightly more than blue. Theory of carbon separation in bitumen paints under light. Lithophone changed. Varnish keeps out oxygen. Linseed oil bleaches, due to action of light on green chlorophyl.

11. Gebhard: Zeit. fr. Farb. Industrie (1909), 7, 299.

Cause of action of light on colors.

12. Bolis: Rev. gen. mat. color. (1909), 12, 289.

Fastness of dyes to light. Decreased by moist air. Less with blue than with red rays. Vacuum little or no action.

13. Huble: Wiener Mitth. (1909), 14, 268.

Glycerol increases light sensitiveness of some dyes five hundred fold.

14. Immerheiser: Text. Farb. Ztg. (1910), 7, 457.

Fastness of coal tar colors.

15. Gebhard: J. Soc. Dyers and Colorists (1910), 26, 173; (1910), 25, 276, 304; Z. angew. Chem. (1910), 22, 2484.

Bleaching of dyes by light depends on (a) oxidation, and (b) formation of peroxide hydrates.

16. Weigert: Ber. (1910), 43, 164.

Some dyes in oxygen-free nitrogen under light show pressure and color changes.

17. Gebhard: Ber. (1910), 43, 751

Defends oxidation theory against Vogel and Wiegert.

18. Gebhard: Z. angew. Chem. (1910), 22, 1890.

Broadens oxidation theory. Shows that O-H and S-H groups decrease fastness and NO_3 group increases fastness.

19 Gebhard: Färber-Ztg. (1910), 21, 95.

Disputes Witt's hypothesis of dyestuffs absorbing and transforming long to short waves capable of producing chemical change.

20. Krais: Z. angew. Chem. (1911), 24, 481.

Modern light; fast wall paper guaranteed for five years. Colored by protected metal powders.

21. Krais: Chem. Ztg. (1911), 35, 146.

Fastness of coal tar dyes in paints.

22. Gebhard: Chem. Ztg. (1911), 35, 273, 290.

Light in relation to chemical action. Influence of wave-length, intensity, catalyzers, and photo chemical after-effect.

23. Gebhard: Färber-Ztg. (1911), 22, 6, 26.

The present method of testing fastness of colors with daylight is unsatisfactory, due to varying atmospheric conditions. Gebhard proposes using a cabinet with both enclosed arc and mercury quartz arc. The change of color whether fading or change to other tint is to be recorded by orthochromatic photography with a light-filter of same color as original dyeings.

24. Scheurer: Bull. soc. ind. Mulhouse (1911), 80, 324.

The mercury quartz arc, with dyes protected against ozone, gave results different from sunlight. Benzo colors were hardly faded by sunlight, but in 24 hours by the Hg. quartz arc. Indigo resisted Hg. quartz arc light better than sunlight.

25. Valenta: Photo. Rundschau (1911), 25, 56.

Sensitizing action of thiosinamine, etc.

26. Gebhard: Färber-Ztg. (1911), 21, 253, 1910.

The oxidation theory of fading is experimentally confirmed. Permanency of dyeing affects permanency of the fiber. $CuSO_4$ improved the lightfastness of dithioalkyl-thioindigo and prevented at the same time the weakening of the fiber.

27. Kummell: Z. wiss. Phot. (1901), 9, 54.

Bleaching is the result of oxidation. H_2O_2 and many sensitizers are studied.

28. Bacon: Philipp. J. Sci. (1911), 5, 281.

The reaction of oxalic acid and uranium salts under light is investigated as to factors significant in dye fading. H_2O_2 factor, concentration Ur., temperature coefficient, etc., are reported on.

29. Schwezow: Z. wiss. Phot. (1911), 9, 65.

Small temperature coefficients of bleaching of dyes.

30. Dosne: Rev. gen. Mat. color. (1911), 14, 193.

An attempt to measure the changing intensity effect of sunlight.

31. Neuberg: Biochem. Z. (1911), 29, 279.

Iron salts act like those of uranium on organic compounds under light.

32. Krais: Z. angew. Chem. (1911), 24, 1302.

A test paper is arranged to measure the varying chemical action of the sunlight. Sun hours were shown to vary 100 per cent from "bleach hours."

33. Gebhard: Z. angew. Chem. (1911), 24, 1807, 2426.

Criticism of Krais' proposal. Sunlight varies in color and composition, and system is clumsy. A list of dyes, decomposed chiefly by red and yellow light, is given. Also a list for short waves and for long and short waves.

34. Klemperer: Färben-Ztg. (1911), 22, 209.

The three primary colors are measured as to change by Kallab app. and plotted against time.

35. Maddox: World's Paper Trade Rev. (1911), 56 392.

·Sunlight greatly deteriorates colored papers.

36. Eibner: Chem. Ztg. (1911), 35, 753, 786.

Tests of paints. Acceleration of effects with certain zinc compounds.

37. Gebhard: Phot. Korr. (1912), 58, 634.

Methylene blue with glycerol or HCHO bleaches in reduction by sunlight more rapidly in vacuo.

38. Gebhard: J. prakt. Chem. (1912), 84, 561.

Relation between the sensitiveness to light and the constitution of dyes.

39. Bancroft: Orig. Com. 8th Intern. Congr. Appl. Chem. (1912), 20, 59.

Permanency of painting. The color change of pigments caused by light is usually an oxidation. A drier in the oil may cause reduction of the pigment. Rapid tests for fastness to light may be made with solution of peroxides and persulphates.

40. Bancroft, Elsenhost, Grant: Orig. Com. 8th Intern. Congr. Appl. Chem. (1912), 20, 91.

Rapid testing of bleaching action of peroxides, etc., is suggested as a qualitative test of the stability of dyes.

41. Gebhard: Z. angew. Chem. (1912), 23, 820.

The formation of peroxides under action of light on dyes is shown by chemical tests. The limited action in dry air is apparent, since the peroxides thus formed bleach just as rapidly as soon as moisture is introduced.

42. Krais: Z. angew. Chem. (1912), 23, 1206.

Coal-tar dyes on carpets, embroidery cotton, resist light better than natural plant dyes. No light-resisting dyes have been found for paper or wood.

43. Valenta: Chem. Ztg. (1912), 33, 1165.

Fastness to light and behavior of different coal-tar dyes taken as printing colors.

44. Krais: Z. angew. Chem. (1913), 25, 2193.

Out of 63 coal-tar dyes, 40 were good as to light fastness and 11 were as satisfactory as the best mineral colors. Some dyes were found to be fast when exposed alone, but were faded when mixed with "blanc fixe." Tests of water colors behind glass, using "bleaching hours" method.

45. Krais: Z. angew. Chem. (1913), 26, 74.

Tests in oil of light fastness of coal-tar dyes. No difference between behind glass and in open, for oil colors. Some 20 coal-tar dyes were as stable as the best mineral pigments.

46. Eibner and Gerstacker: Chem. Ztg. (1913), 37, 137, 178, 195.

Action of light on Turnbull's blue, etc.

47. Harrison: J. Soc. Dyers and Colorists (1913), 28, 225.

Besides oxidation, reduction theory is also used for several types of change under the action of light.

48. Gebhard: Chem. Ztg. (1913), 37, 601, 622, 638, 662, 679.

Criticizes Harrison's results and defends oxidation theory. Under the conditions of daily life, the fading of dyeings is due to oxidation process. The reducing properties of fibers are, contrary to Harrison, without influence upon the light-fastness of dyeings.

49. Gebhard: Z. angew. Chem. (1913), 26, 79.

Oxidation in the light may be wholly different from that in the dark, even when the same oxidizing agent is used. Light of different wave lengths may cause the oxidation to proceed in different ways. Hence the limitations of the chemical method proposed by Dr. Bancroft.

50. König: Färben-Ztg. (1914), 24, 366.

Influencing the light fastness of dyeings.

51. Official report of committee on fastness of dyes of the section for dyes and textile industries of the Society of German Chemists. Z. angew Chem. (1914), 27, 57.

52. Tauber: Färben-Ztg. (1914), 19, 475.

Methods of testing the injurious effect of zinc whites on the stability of water colors, on exposure to light.

53. Ragg: Färben-Ztg. (1913), 18, 578.

The behavior of white zinc, white lead, and lithophone in paint colors.

54. Engelmann: Ger. Pat. 264,904 of 1912.

Manufacture of a lithophone stable to light.

55. W. J. O'Brien: Jour. of Phys. Chem. (1915), 19, 113.

A study of lithophone. The light of a 25A Macbeth printing lamp with flame carbons was found more satisfactory for most purposes than sunshine.

56. Bancroft: Jour. of Phys. Chem. (1915), 19, 145.

The fastness of dyes to light, water, etc., is discussed. "The whole question of fastness to light is in a very bad way, because so little systematic work has been done. About all that I can hope to do at present is to point out how much we do not know in the hope that some enthusiastic person will fill in some of the gaps in our knowledge some day." Discussion is given of a number of protective factors and references to literature.

57. British Commercial Gas Association: Abstracted, American Gas Light Journal (22 Feb., 1915), 102, 116.

The influence of temperatures, products, and light of gas illumination is found to be very small, compared to a little daylight.

58. Crookes: Dyeing and Calico Printing. Published 1874, Longmans, Green & Co., pages 655 to 661.

A valuable discussion is given of the influence of light on all kinds of colors. Madder should be ground in the dark. Mordants also, especially the preparations of iron and tin, lose their affinity for the fiber, and are rendered worthless by even a short exposure to direct sunlight. "Out of 60 typical dyes, only three resisted the sunshine of three summer months. Over two-thirds were changed in less than 8 days."

59. Laycock, Rawson, Gardner: A Dictionary of Dyes, Mordants, etc. Published 1901, J. B. Lippincott Co., page 139.

Summary of Brit. Assoc. Report over five years' experiments of action of light on dyes.

60. Barrows: Electrical Illuminating Engineering. Published 1908, McGraw Publishing Co., page 150.

Comparison of ultraviolet light of mercury arc and several months of tropical sunlight.

61. Zerr, Rubencamp, Mayer: "A Treatise on Color Manufacture." Published 1908, J. B. Lippincott Co., page 71.

"Exposure to the direct sunlight is a drastic test, under which fugitive colors will show a remarkable change in the course of a day."

62. Zerr and Mayer: "Tests for Coal-Tar Colors in Aniline Lakes." Published 1910, J. B. Lippincott Co., page 227.

The fastness to light of coal-tar color lakes.

63. Fay: "Coal-Tar Dyes." Published 1911, D. Van Nostrand Co., Indigo—5,000 years old, page 375.

64. Knecht, Rawson, and Loewenthal: A Manual of Dyeing. Published 1910, J. B. Lippincott Co., pages 743 to 748.

There is an excellent discussion, with references, in this book. The diversity of testing methods is brought out. Some test by exposure to weather, some under glass, some to diffused sunlight, and some to combined skylight and sunlight. Some test in a horizontal position and some in a vertical. "For exact measurements, however, it would be necessary to measure the average intensity of the sun's rays during the different seasons of the year and for different climates." The atmosphere in town is more acid and in the country more alkaline. Alcohol vapors enormously increase the action of light. The light complementary to the dye has more action. Blue, of course, tends to affect more dyes than the red. The most favorable condition for bleaching by sunlight is one which is hot, moist and alkaline. A dye is called fast if not materially altered on southern exposure under glass for one summer month.

65. Sheppard: Photo-Chemistry. Published 1914. Longmans, Green & Co., page 431.

Photolysis of dye-stuffs.

66. Potter: Trans. Am. Electrochem Soc. (1907), 12, 218.

Sunlight and corrosion of metal by different paints.

67. Plotnikow: Photochemische Versuchstechnik. Published 1912, Leipzig. Akademische Verlagsgesellschaft m. b. H. pages 192, 193, Laws of Dye Fading. Page 273.

Temperature Coefficient of Light Reactions and 13 references to the literature on the same.

68. Toch: Materials for Permanent Painting (1911).

69. Mees: Discussion of Ives' Paper on Light Filters for Use in Photometry. Trans. Ill. Eng. Soc. (1914), 9, p. 996.

Satisfactory progress is being made in the cultivation of cotton in the German possessions in East Africa, where the natives have shown themselves well fitted for this occupation. American Upland is preferred to Egyptian varieties, as the former has proved better able to withstand disease and the effects of unfavorable weather; the American plant also has a larger yield of lint. A special report recently issued by the German Imperial Governor of East Africa states that two districts along the coast, Rufiyidelta and Lindi, are exceptionally well suited for cotton culture; the plant also grows well in the Muansa district in the interior, but in this region the effects of the so-called Masuta disease are noticeable. The number of colonial stations established by the Government for educational and experimental purposes in the growth and use of cotton has been increased. It is expected that selected seed from these stations will soon be available in quantities sufficient to meet the entire demands for planting purposes. In the districts controlled by Europeans, progress has also been made in raising cotton. Many private planters, largely through the activity of the cotton stations, enlarged the planting of the Egyptian varieties, but it is generally conceded that Upland cotton, especially Nyassa Upland, produces very satisfactory results.

Secretary Redfield recently approved the award of the contract for the construction of a chemical laboratory building for the Bureau of Standards, Department of Commerce, to Wells Bros. Co., of New York, whose bid was $188,556. The contract has now been signed, the contractors have filed the necessary bond, and the construction work is to be commenced immediately. Dunn & Deming, of Washington, D. C., are the architects.

The new committee appointed by the executive government at Manila to study the copra or cocoanut-meat industry in the Philippines is making its investigations. Attention has been called to the higher quality of copra produced in Ceylon, and it is estimated that if the Philippine copra were cured as carefully it would bring $1,500,000 more income.

METALLURGY

THE HARDNESS OF SOLID SOLUTIONS.*

By DR. CECIL H. DESCH.

Most of the recent contributions to the subject of the hardness of metals have dealt with the hardening produced by quenching, by cold-working, or by surface flow. A complete theory of hardening must, however, also take into account the facts relating to the hardness of solid solutions (mixed crystals). It is well known that the hardness of the alloys of a pair of completely isomorphous metals, such as gold and silver, is not an additive property, but is always greater than the hardness calculated by the rule of mixtures. For example, in the instance just mentioned an alloy containing equal weights of gold and silver is about twice as hard as either of the component metals, and alloys of gold and copper, or of copper and nickel, present similar maxima in the curve of hardness. When the two metals for a compound which enters into solid solution with both of its components, the curve of hardness presents a downward-directed cusp at the composition of the compound, with a maximum on each side. This case is very clearly exemplified by the remarkable alloys of cadmium and magnesium, the cusp corresponding with the compound MgCd. The same conditions may be traced, although complicated by other factors, in the alloys of copper with zinc, and tin and of silver with magnesium.

The hardness of the elements is a periodic function of the atomic weight the curve of hardness hearing a close resemblance to the curve of atomic volume. Benedicks found that the hardness is closely proportioned to the atomic concentration, that is, the number of atoms in unit volume, expressed by the quotient of the density by the atomic weight, and the rule has been extended to compounds by employing the mean atomic weight (molecular weight divided by the number of atoms in the molecule). A very close agreemnt is not to be expected, in view of the numerous sources of error in determining the relative hardness of different solids. It has been shown that the most considerable deviations are found in substances which exhibit very perfect cleavage, and therefore yield to an abnormal extent when submitted to the usual methods of testing.

A closer agreement between theoretical and experimental values for the hardness has been obtained by the application of Van der Waals' equation to solids. In the equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$\frac{a}{v^2}$ is termed the internal pressure, and an arrangement of the elements in order of their pressure coincides almost completely with the order of hardness. This is illustrated by the following figures, extracted from a table given by Traube, to which the values of the atomic concentration have been added:

Element.	Atomic Concentration.	Internal Pressure (Megabars).
Potassium	0.022	8,190
Sodium	0.042	18,500
Lead	0.055	51,500
Tin	0.061	68,700
Copper	0.140	236,100
Nickel	0.151	306,300
Carbon (diamond)	0.290	5,458,000

On both of these views, the increased hardness of solid solutions is due to an increase of pressure, regarded by Benedicks as osmotic pressure and by Traube as internal pressure due to dissolved carbide in a quenched steel containing 0.89 per cent of carbon to be 137.8 atmospheres, assuming the carbide molecule to be Fe$_3$C, or 68.9 atmospheres, assuming it to be Fe$_8$C$_2$.

These relations make it clear that the problem of hardness is connected with that of the close packing of the atoms or molecules in a solid. Different views have been taken as to the nature of the packing in the metals. According to Barlow and Pope those metals which crystallize in the regular system are represented by the cubic closet-packed assemblage of equal spheres. "It must not, however, be concluded that for this reason all the spheres composing the structure are identically treated in the packed assemblage; some, selected homogeneously, might be differently treated from others and the assemblage yet exhibit holohedral, hemihedral, or tetratohedral symmetry of the cubic system according to the particular type of homogenous distributlon of the preferentially treated spheres."

In the simplest cubic arrangement, each sphere is in contact with twelve others, and compression continued until the intervening spaces are completely obliterated converts each sphere into a regular rhombic dodecahedron. On the other hand, Sollas assumes comparatively loose packing of the component spheres.

It has recently been found possible to apply an experimental test. The discovery that the reflection of X-rays by crystals bears an intimate relation to the internal structure of the crystal provides a means of investigating this structure. So far one metal has been examined in this way. Crystals of native copper, when submitted to the action of X-rays, reflect the latter at certain angles, indicating that the unit of the space-lattice for this metal is the face-centered cube. This structure corresponds with the simple closest-packed cubic arrangement, in which every atom, regarded as a sphere or parallelohedron, is in contact with twelve similar spheres or parallelohedra. Whether closet-packing is absolutely essential to the interpretation of the experimental results is, however, not quite clear, and the opinion of an expert crystallographer on this point would be of interest.

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*From Transactions Faraday Society, Vol. 10, May, 1915.

There are many types of crystalline solid solution, and it will be advisable to consider only the simplest of these at present. The most important pairs of metals which form complete series of solid solution with one another are: Gold-silver, gold-copper, copper-manganese, copper-nickel, gold-platinum, platinum-iridium, and antimony-bismuth. All but the last of these pairs crystallize in the cubic system. The pair magnesium-cadmium may be omitted on account of the complication introduced by the compound MgCd. This leaves six pairs which are fairly well known, and of which the members crystallize in similar simple forms. In each case, the two components have nearly equal atomic volumes; and these volumes are small, gold, silver, copper, manganese, nickel, and the platinum metals all occuring at or near the minima on the periodic curve of atomic volumes. The following values may be adopted.

Au	10.202	Ni	6.64
Ag	10.233	Pt	9.06
Cu	7.077	Ir	8.61
Mn	7.44		

The case of the alloys of gold and silver may be regarded as typical. The atomic volumes of the two metals are very closely similar. The internal crystalline arrangement of silver and gold has not yet been determined by the method employed for copper, but the external crystallographic characters are almost identical, and it is probable that an exactly similar space-lattice will be found to fulfill the conditions of all three metals. The difference between the atoms of gold and silver is then so small that the two space-lattices should interpenetrate freely without appreciable distortion, and the solid solutions of the two metals should be crystallographically indistinguishable from their components. The available data are too scanty to decide whether this is actually the case. The native alloy, electrum, is described as similar. It is hoped that an examination of the alloys by the X-ray method may shortly be undertaken. The fact that the freezing-point and solodus curves of the gold-silver system approach so closely to a straight line also suggests that the mixture is of a very simple type, whilst the specific volume is strictly proportional to the concentration, the greatest deviation from the mixture rule being only 0.2 per cent. Diffusion of silver into gold takes place very readily; for example, a gold wire, 0.46 mm. in diameter, was coated electrolytically with silver until the compound wire contained 62.7 per cent Ag. The electrical conductivity was determined, and the wire was then heated at 900°. The conductivity gradually fell, and reached a final value after 120 hours. The diameter of the wire was then 0.98 mm., and its conductivity was that of a homogeneous alloy of the same dimensions and composition.

These facts indicate that the solid solutions of gold and silver are of a very simple character. Nevertheless, the hardness of the alloys is considerable, attaining a maximum value which is twice that of the pure metals, whilst the electrical conductivity is correspondingly diminished, passing through a minimum. Of the two explanations which first suggest themselves, an alteration in the closeness of packing seems improbable in view of the equality of the atomic volumes throughout the alloys. There remains the assumption of a condition of internal strain. On this view, the hardness of a solid solution is due to the same cause as that of a fold-worked metal, namely a disturbance of the crystalline structure, giving rise to an amorphous or irregular arrangement of the atoms or molecules, or at least, if the conditions be regarded from a kinetic point of view, to a constraint of the atomic or molecular motions.

This is an aspect of the problem which has been treated by Dr. Beilby, but has received very little attention from other writers.

According to Tammann, the increased hardness of solid solutions is due to the fact that "the attractive force between two different molecules is always greater than the attractive force between two similar molecules in the same mixture." It is therefore to be expected that the attraction, and consequently the hardness, should be a maximum in the solid solution containing equal molecular proportions of the two components, and this rule is approximately fulfilled in the case of several of the series investigated by Kurnakoff and Schemtschuschny. It may be noted that the rule is confirmed by application to cases in which an intermetallic compound is formed. Thus, the compound MgCd forms a continuous series of solid solutions with both of its components. The maximum hardness is not that of the compound, although this is harder than either component, but the curve plotted with atomic percentages presents two maxima, approximately midway between Mg and MgCd and between MgCd and Cd respectively. These are the two compositions at which there is the greatest admixture of foreign molecules.

Direct evidence of a constrained condition of the molecules of a solid solution, or of a disturbance of the internal crystalline structure, is not easy to obtain in the case of metals, but the conditions are more favorable in that of isomorphous salts. These salts frequently exhibit "optical anomalies," indicating the presence of internal strain, and such a condition is often assumed to be usual. It is, however, by no means necessarily the case. In his very careful work on isomorphism. Retgers has shown that the anomalies do not always occur, and has used their absence as one of tests of the homogeneity of isomorphous "mixed crystals" required for investigations of density. The most conspicuous examples of crystals exhibiting optical anomalies are those of salts crystallizing from solutions containing dyes. Here there is no question of the interpenetration of space-lattices, and the production of a strain in the crystals is readily comprehensible, but where two salts of almost identical molecular volume are concerned, it seems probable that Retgers' view is correct, and that optical anomalies are absent when sufficient care is taken to conduct the crystallization slowly and in presence of a large excess of the saturated solution.

It is usually stated, also, that solid solutions crystallize less readily, or yield less perfect crystals, than pure substances. This is not invariably the case, but the fact has been observed so frequently that it must be regarded as evidence for a certain disturbance of crystalline structure in solid solutions.

The heat of formation of solid solutions has hitherto been determined only in the case of isomorphous salts, and then by an indirect method, the heat of solution of the solid solution in water being compared with that of a mechanical mixture of the components in the same proportions. The pairs of salts which have been examined satisfactorily by this method—$NaCl$-KCl, $NaBr$-KBr, NaI-KI, KCl-KI, $NaNo_2$-$NaNO_3$—all give results indicating a negative heat of formation for the solid solution. For two of these pairs, namely KCl-KBr, and KBr-KI, the hardness curve, as determined by measuring the pressure required to produce flow through an orifice, passes through a maximum not far from the middle of the series.

It will be seen that the data which are available for drawing a conclusion as to the hardness of solid solutions, even in such a simple case as the alloys of gold and silver, are very scanty. The complete proportionality which exists between density and composition by volume (or between specific volume and composition by weight) seems to exclude any important differences in the closeness of packing. There remains a difference in the attractive forces between the atoms—what is usually called internal pressure, and even here it is not easy to realize why the attractive force between gold and silver should be twice as great as between gold and gold or between silver and silver. A distortion of the space-lattice, producing a more or less irregular arrangement, is only compatible with the conservation of the original density of the assumption of some form of packing which is not the closest possible. It would therefore seem that the solution of the problem must be sought from the crystallographers, whose newly added resources enable them to determine the direction of the planes of closest packing within a crystal, and the actual form of the space-lattice.

MOLTEN ZINC AS A REAGENT FOR THE MACROSCOPIC ETCHING OF IRON AND STEEL.*

By JESSE L. JONES.

The microscopic examination of steels after polishing the surface of small samples and then etching with various reagents, has been brought to a high degree of excellence. Not so much work has been done, however, in rendering visible on a large scale the porosity, lack of homogeneity in composition, hair cracks, blisters, seams, overlaps, slivers and other defects in steel that the rolling or forging treatment has rendered difficult to detect by ordinary visual inspection.

A large user of machinery steel forgings recently obtained, from various steel works, a number of 15-in. ingots and sawed them in half longitudinally. The sawed surfaces when polished showed hundreds of large air bubbles and innumerable small ones, as well as hair cracks in the case of ingots that had stuck in the molds and had not been allowed to shrink freely for this reason. The subsequent mechanical treatment that such ingots receive never altogether removes the porosity and other defects due to the enclosed or occluded air and gases in them. This was proved experimentally by spinning a glass rod about a platinum wire 0.040 in. in diameter, so as to give it an impervious coating of glass. The wire thus coated was heated electrically to a red heat in a vacuum and bubbles of air or gas continued to force their way through the glass for several days.

In the making of low, medium and high-carbon steels in the open-hearth furnace there is quite a divergence in practice, some makers adding to the steel while in the furnace the ferro-alloys used, while others add them to the steel as it runs into the ladle. Some makers recarbonize while others "bring down" the pig-iron and steel-scrap mixture to the required carbon.

In the case of alloy steels, such as high-speed tool steels which contain notable amounts of tungsten and other metals with high melting points, the tendency to lack of uniformity is more marked than in ordinary steel. These steels are usually made by the crucible process. Plumbago crucibles holding from 90 to 160 lb. (these may be taken as the minimum and maximum sizes used) are placed in regenerative furnaces which each accommodate ten crucibles. These are previously charged with the steel mixture, which consists of sheared muck bar (made from low-phosphorus or Bessemer pig iron), ferro-tungsten, ferro-chromium, ferro-manganese, ferro-vanadium, cobalt, etc. The crucibles are tightly sealed so as to keep out the air as much as possible. An effort is made to keep the temperature at the bottom of each crucible at about 3,100° F., or several hundred degrees higher than the top, in order to "lift" the tungsten from the bottom of the crucibles, its high specific gravity and high melting point rendering this necessary. To prevent an undue amount of carbon being taken up by the steel, the crucibles are clay-lined or clay-washed and a quantity of crushed soft red brick or similar material is added to glaze over the surface of the crucibles. Even with these precautions the carbon in the various crucibles is different. It has been found that if the crucibles are poured one by one into an ingot mold, a "calico" ingot or one of varying carbon content is produced. Hence the crucibles are emptied into a steel ladle and this is bottom-tapped into the ingot mold, thus giving a more homogeneous ingot.

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*From a paper presented before the American Society for Testing Materials.

It is evident from the above review of the processes of steel making that they are far from perfect, and while chemical analysis, microscopic examination and the various physical tests such as tension, Brinell hardness, etc., are more or less satisfactory for the inspection of steel, any improvemnt in the methods of macroscopic examination would be very desirable. Such an improvement seems to have been found in etching the steel with molten zinc.

The writer had ocasion recently to ascertain the relative value of ingot iron, Norway iron and open-hearth steel for making pots for hot galvanizing. Bars 10 by 1¼ by 5/16 in. of each of these materials were suspended in the molten zinc in a 14-ft. galvanizing pot, by means of iron wires. The samples were placed at the end of the pot because there was no firebox at that point, and hence if one sample happened to be nearer the end of the pot than another it would not for that reason be subjected to a higher temperature. Later, similar samples of carbon tool steel and high-speed steel were added. On taking the samples from the molten zinc the mass of dross surrounding them could be broken off while still hot by blows from a hammer, and the coating of metallic zinc removed by immersion in dilute sulphuric acid, which does not attack the steel as long as any zinc remains. Table I gives the results of this experiment.

The high-speed steel had its surface deeply pitted and grooved at some points, but the rest of the surface was scarcely attacked at all. The spots that were attacked are probably areas high in carbon, due to imperfect alloying of the ferro-tungsten and other additions. These additions are usually high in carbon and also of high melting point. Hence they do not diffuse very rapidly and the resulting mixture may not be homogeneous.

TABLE I.—LOSS OF BARS ON IMMERSION IN MOLTEN ZINC.

Material.	Time of immersion, hours.	Total loss, per cent.	Loss per square inch in 24 hours, per cent.
Ingot iron	168	2.95	0.012
	336	6.78	0.014
	672	12.79	0.013
Norway iron	168	3.73	0.016
	336	7.46	0.016
	672	14.22	0.014
Open-hearth steel	168	3.93	0.017
	336	7.57	0.016
	576	12.80	0.016
	720	15.76	0.016
High-speed steel	24	7.39	0.199
Carbon tool steel	48	21.57	0.348

The carbon steel was not only eaten away to a high degree, but it also showed a curious shelly structure, the edges being cut away and apparently concentric layers of steel exposed to view as if the steel during the rolling process had not been sufficiently plastic to fill out the grooves in the rolls, and these edges, either because of minute fissures or on account of not being sufficiently compressed to remove porosity, had readily dissolved in the molten zinc.

THE HARDENING OF METALS.*

By G. T. BEILBY.

The subject may be conveniently arranged under the following sections:

1. Hardening of the pure ductile metals results from any form of working.

2. Hardening of the pure ductile metals may result from their mixture with each other or with non-metallic elements, e. g., hydrogen, nitrogen, carbon, etc.

3. When these mixtures are ductile they, like the pure metals, may be further hardened by cold working.

4. Certain of these mixtures have the property of hardening by chilling.

The sudden drop in temperature which results from chilling may act in two ways:

(a) It may stereotype the form of chemical combination or of structure, crystalline or non-crystalline, which is in the condition of equilibrium at the temperature at which chilling begins.

(b) It may set up contraction strains within the cooled mass. These strains may be wholly or in part either within or beyond the elastic limits. When the strains exceed the elastic limit and permanent deformation occurs, then hardening may result as in 2.

As a means of throwing light on the molecular structure of solids the study of the phenomena under Section 1 has appealed to me very strongly, because of certain great advantages which are inherent to this side of the subject. Chief among these advantages is the fact that in a pure metal we have only one kind of chemical or ultimate atom, and that in certain ductile metals the chemical molecule is monatomic. It follows that in dealing with a given mass of metal either "hard" or "soft," we are dealing with the same number and kind of atoms or molecules occupying practically the same volume in whichever state the aggregate is found. In a problem which is essentially a physical one it is no small advantage to know with certainty that chemical questions have been completely excluded. The ease and certainty with which the pure ductile metals, in particular gold, silver and copper, can be passed from one state to another, soft to hard, or hard to soft—is an important practical advantage in experimental work. Further, these metals recrystallize from the hardened state at temperatures which are so much above the ordinary atmospheric temperature that their permanence in the hardened state is assured, while the fact that their recrystallizing temperatures are more than 800° below the liquefying point at once removes any suspicion that the mobility of the atoms or molecules, which is a necessary feature of recrystallization, is of the same degree as the mobility of the liquid molecules.

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The problem of the two states in the pure ductile metals can be stated thus:

A centimetre cube of metal in the hard state containing x ultimate atoms or molecules has certain well-marked physical qualities. This cube when heated to about 300° loses the characteristic qualities, so that from the physical point of view it might be a different metal. It still contains x ultimate atoms or molecules, and the volume they occupy is still practically a centimetre cube. As the number of molecules and the space they occupy are both constant, the intrinsic cohesive force of the aggregate is also constant, though the effective cohesive force, on which the greater or less rigidity of the aggregate depends, will vary (1) with changing energy conditions, and (2) with the relative positions of the atoms or molecules to each other if they possess polarity. With respect to energy changes in passing from one state to the other it has been conclusively proved that there is a considerable storage of potential energy in the hardened state and that this storage is associated with a marked reduction in the vibrational freedom of the atoms or molecules. We may picture this as due to the molecules being so pressed together that they curtail each other's vibrational freedom. It is not, however, quite correct to speak of their being "pressed" together, seeing that the force which enables them to hold each other more closely is their own attraction or cohesion.

From the first it has appeared to me most probable that the atoms or molecules do possess polarity, either as an intrinsic property or more probably as a property developed by heat vibration, and that the metal in the hard vitreous condition is truly amorphous, inasmuch as its atoms or molecules are crowded together heterogeneously as regards their polarities. The temperature-elasticity curves, as well as the curves of thermoelectric potential, show the existence of distinct stages in the recovery from strain as the annealing temperature is raised. There is a comparatively quick relief when the metal is heated to 100°, followed by a slower rate till the crystallizing range is reached. Over the comparatively short crystallizing range the relief is so rapid that it definitely suggests that a new type of structural change has set in. The microstructure shows that this corresponds with (1) the disappearance of the characteristic hardened structure, (2) the appearance of minute detached crystalline aggregates, and (3) the apportionment of the whole mass among well-developed crystalline grains.

It seems natural to picture the earliest steps in the relief of strain as due to the energizing effect of rising temperature on the molecular vibrations. A slight general expansion of the mass will occur, and the potential energy released by this expansion will augment the kinetic energy of the vibrating molecules, but not to the point at which they can free themselves sufficiently to enable them to take their true orientation under the influence of the crystalline nuclei in the mass, which always persist in spite of the most drastic deformation. When the temperature is raised to the beginning of the crystallizing range we may suppose that a proportion of the molecules have attained the necessary amplitude of vibration to set them free to orient, and with rising temperature further progress towards complete orientation and re-orientation takes place over the remainder of the crystalline range till the whole mass is apportioned into crystal grains, each with its own orientation. Re-orientation of the freely vibrating molecules must certainly occur as the larger grains impress their orientation on their smaller neighbors or on other partially oriented aggregates.

In this type of recrystallization at a temperature which may be as much as 800° or 1,000° below the liquefying point, it is not necessary to suppose that there is any transport of molecules from crystal to crystal. Orientation of the molecules only requires that they shall turn in situ in response to the cumulative vibration of a more powerful crystal.

The foregoing illustration shows the remarkably self-contained nature of the problems of Class 1, as well as their almost elemental simplicity, at least in outline. The qualitative differences between the two states are not disputed. That these are due to the intrinsic properties of the pure metals is disputed. That these are due to the intrinsic properties of the pure metals is proved by the fact that these differences become more sharply defined as metals of greater purity are used. Most of these differences lend themselves to exact measurement, as, for instance, the hardness, rigidity, or mechanical stability, the electrical conductivity, the thermoelectric potential, the energy of solution and the elasticity by the acoustical method. The microstructure can be recorded by photography, though we need to remember that no photographic records, however perfect, can take the place of direct study with the microscope. In every case the thermally stable crystalline state supplies a fixed standard of reference. No uncertainty attends the passage of the pure metal from the hard to the soft fully crystallized state, neither is there any uncertainty in the reverse change from soft to hard by cold working, but the particular mode by which this working is effected, and the extent to which it is carried, mainly affect the ultimate texture of the hardened metal and therefore also its mechanical qualities.

This question of texture has not received the attention which it deserves, yet it absolutely stares us in the face in the sections of drawn or rolled work. It may be so coarse that it is clearly seen by the unaided eye, or so minute that the highest powers of the microscope are needed to resolve it fully, but whatever the scale of magnitude the texture is always true to its type.

It is the existence of "texture" in cold-worked materials which makes the value of all density determinations of hardened metal so uncertain. If cold working brings some of the molecules so close together that they interfere with each other's freedom of vibration it is clear that if the volume of the hardened mass is not less than that of the corresponding crystalline mass, other groups of molecules must spread themselves out in wider spacing.

To return to the centimetre cubes of our illustration, we have seen that the difference between the two must be due to some difference in the arrangement of the atoms or molcules in the given space. The greater hardness or rigidity or the hard cube shows unmistakably that the atoms or molecules move over each other with much less facility than they do in the soft cube. There is also an increase of tenacity which points in the same direction and in addition confirms the suggestion that the cohesion of the atoms or molecules is being used with much greater effect. It must be admitted that these are facts, explain them how we may. But there are more facts about the hard cube. The elasticity of its atoms or molecules has been seriously impaired. The acoustical test of elasticity which Mr. McCance has used, and the first use of which in this connection he attributes to M. Robin in 1911, had already been extensively used by me and was described in 1907.* The coincidence of the elasticity curves with the e.m.f. and tenacity curves was also demonstrated and discussed in the same paper. The steps in the release of elastic strain and their correspondence with the course of recrystallization were also demonstrated and discussed. Two sets of facts have therefore been established; the mechanical properties show that the atoms or molecules are holding each other more firmly, while the physical tests show that a state of elastic strain exists throughout the aggregate. My interpretation of the facts is that the second set confirm and emphasize the first set in showing that in the molecular structure of the hard cube a proportion of the molecules are either drawn more closely together by their intrinsic cohesion or can come into more favorable action.

Having traced the passage from hard to soft as recrystallization sets in and completes itself over a certain range of temperature, let us now try to follow the reverse operation. If we drop a hammer on the soft cube the change is accomplished at a blow, and no method has yet been devised by which the steps which separate the soft from the hard state can be watched as they occur. The amorphous theory for which I am responsible is that under mechanical disturbance crystalline lamellæ or sheets break down momentarily into the liquid state and instantly resolidify in a vitreous amorphous condition, thereby forming a hard cementing material which binds the disturbed and partially broken-up crystal aggregates together. By carrying out experimental observations on surface flow in metals and other solids it appeared to me that conclusive evidence had been obtained that the intermediate liquid state is a necessary and invariable step in the breaking down of the crystal structure by flow. It further appeared that the type of internal structure, the "texture" of cold-worked metals, strongly confirmed the view that the new aggregate shows all the indications of being a concreted mass. This view, that there is an actual liquefaction and resolidification, appears to account in a satisfactory way for the vitreous character of the flowed metal, for it is really the product of a liquid which has been solidified with a rapidity far exceeding that which can be reached by the chilling methods with which we are familiar. This instantaneous cooling is, of course, accompanied by equally sudden contraction, with its accompanying state of elastic strain.

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*Proc. Roy. Soc., A, Vol. 79, 1907, p. 475.

THE DETERMINATION OF SPELTER COATING ON SHEETS AND WIRE.*

By J. A. AUPPERLE.

For many years the Preece copper-sulphate test has been used to determine the amount of galvanized coating on sheets and wire. Committee A-5 on the Corrosion of Iron and Steel reported to the Society in 1911 on this test as follows:

"It is, however, the unanimous opinion of the committee that the well-known Preece copper-sulphate test is unreliable and should be abandoned entirely as a basis of specification with respect to galvanized sheet and plate. In respect to wire, the Preece test has the advantage of being quick and simple, and if carried out in the proper manner yields comparative results of value. In the opinion of the committee, the lead-acetate test is preferable to the copper-sulphate test for determining or specifying the weight of zinc coatings."

The lead-acetate method recommended by Committee A-5 in 1911 yields very accurate and satisfactory results, but the length of time required for making the test seriously limits the scope of its usefulness. The results obtained with the method described in this paper compare very favorably with those of the lead-acetate method.

There is much to be desired in the method of expressing the weight of coating on wire products in order to have an intelligent understanding as to the weight of coating per unit area. It has been customary to express the weight of coating on wire in pounds per mile, while on sheet products the results are usually expressed in ounces per square foot. Obviously, the coating on wire expressed in pounds per mile would have a different meaning for each gage of wire. If the results are expressed in ounces per square foot of surface on both wire and sheets, there will be a better understanding as to the thickness of coating on the respective products. In stating the weight of coating on galvanized sheets it is customary to express the weight based on one surface only, that is, a sheet containing 2 oz. of coating per square foot really contains 1 oz. on each side of the sheet.

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*A paper presented at the meeting of the American Society for Testing Materials, June, 1915.

It is proposed to express the weight of coating on wire in ounces per square foot, and also to use such lengths of wire that the number of grams of coating found will be equivalent to ounces per square foot, without calculation. These lengths must be such that the surface coated is equal to 5.079 sq. in. It is likewise proposed that the samples for determining the weight of coating on galvanized sheets shall be 2¼ by 2¼ ins. (area = 5.079 sq. ins.). The number of grams of coating on a section of this size will also express the weight of coating in ounces per square foot without calculation.

The method for determining the weight of spelter coating consists of using a small amount of antimony chloride in hydrochloric acid (sp. gr. 1.20). Antimony chloride appears to hasten the solution of the coating, and after the coating has dissolved a thin film of antimony plates on the surface of the base metal and retards the solution of iron or steel. Experiments have shown that sheet steel 2¼ by 2¼ ins., which loses 50 mg. in five minutes in cold hydrochloric acid (sp. gr. 1.20), will lose in that time only 1 mg. in the same acid containing 80 mg. of antimony per 105 cc. of acid.

In the proposed method the metal is immersed in the acid only one minute, which is long enough to dissolve several grains of coating, yet the amount of iron or steel dissolved is negligible. The small amount of antimony that plates on the surface of the sample can easily be removed by scrubbing under running water. This method is one of the most rapid and accurate with which the writer is familiar, and a determination can be made in less time than is occupied in making the Preece test.

Sheets.—For determining the weight of coating on galvanized sheets cut several samples 2¼ by 2¼ ins. from various parts of the sheet. These samples, about five in number, should be weighed together and immersed singly for one minute in 100 cc. of hydrochloric acid (sp. gr. 1.20), to which has been added 5 cc. of antimony chloride prepared by dissolving 20 g. of antimony trioxide in 1,000 cc. of hydrochloric acid (sp. gr. 1.20). The same 100 cc. of hydrochloric acid can be used for at least five samples. Five cubic centimeters of the antimony chloride, however, should be added for each sample on account of the antimony being removed from the solution by the iron.

The samples are washed and scrubbed under running water, dried with a towel, and laid in a warm place for a few seconds. The samples are again weighed together and the number of grams lost is divided by the number of samples taken. Each gram corresponds to 1 oz. of coating per square foot.

TABLE I.—LENGTHS OF WIRE TO GIVE GRAMS OF COATING EQUIVALENT TO OUNCES PER SQUARE FOOT.

Gage No.	Diameter, in.	Length for Test, in.	Length for Test, cm.
0	0.340	4 12/16	12.1
1	0.300	5 6/16	13.7
2	0.284	5 11/16	14.5
3	0.259	6 4/16	15.9
4	0.238	6 13/16	17.3
5	0.220	7 6/16	18.7
6	0.203	7 15/16	20.2
7	0.180	9	22.8
8	0.165	9 13/16	24.9
9	0.148	10 15/16	27.7
10	0.134	12 1/16	30.6
11	0.120	13 8/16	34.2
12	0.109	14 13/16	37.7
13	0.095	17	43.2
14	0.083	19 8/16	49.5
15	0.072	22 7/16	57.0
16	0.065	24 14/16	63.2
17	0.058	27 14/16	70.8
18	0.049	33	83.8

Wire.—A small section of the galvanized wire should be stripped in hydrochloric acid containing antimony chloride. The diameter of the black wire should then be carefully measured in order to determine the length of wire, such that the number of grams of coating will represent the number of ounces per square foot of surface. These lengths are given in Table I. In the lighter wires, however, it will be found convenient to use some fraction of these lengths.

The method of making the test is very similar to that outlined for galvanized sheets, except that the wire is first cleaned with carbon tetrachloride or gasoline, and after being carefully weighed is placed in a tall glass cylinder containing hydrochloric acid (sp. gr. 1.20), to which has been added from 2 to 3 cc. of antimony-chloride solution of the same strength as used on galvanized sheets. The reason for using one-half the amount of antimony chloride in the case of wire is on account of taking one-half the area. As previously stated, the coating on galvanized sheets is expressed in ounces per square foot, considering one side only, when in reality this amount of coating represents two square feet of surface. After immersing the entire length of wire for one minute it will be found convenient to pour the acid solution into another tall cylinder in order to facilitate removing the wire. The wire is then scrubbed under running water, wiped, thoroughly dried in a warm place for a few seconds and again weighed. Each gram lost corresponds to 1 oz. of coating per square foot. For direct comparison with the weight of coating as expressed on galvanized sheets, this figure should be doubled.

A NEW VANADIUM STEEL.*

To meet the requirements for a steel of greater strength for locomotive axles and forgings, the railroads in the past have turned to heat-treated carbon and heat-treated alloy steels, particularly chrome-vanadium steel. In the former, heat treatment has caused an increase of 20 to 25 per cent in elastic limit over the annealed steel, but in chrome-vanadium axles an increase of 100 per cent in elastic limit over the same steel annealed is specified and obtained by heat treatment. The relative cost of chrome-vanadium forgings is high, however, and can be only partly offset by taking advantage of the greater strength to reduce the section and weight. Lack of heat-treatment equipment has been one obstacle to the adoption of heat-treated forgings in railroad shops, particularly in repair work.

In view of the reduced cost of vanadium in the past year the American Vanadium Company resumed the investigation and study of the application of vanadium to simple carbon forging steels, which was dropped about 12 years ago. As a result the company has developed a type of carbon-vanadium steel which without heat-treatment other than annealing meets the requirements specified for heat-treated simple carbon steel forgings of like section. These results are obtained, it is stated, from steel with lower carbon than is generally used to obtain the physical requirements for heat-treated carbon steel locomotive axles and forgings. The cost of this steel is only a little higher than simple carbon steel.

In the table which follows are given results of tests on axles and connecting rod forgings from this new type of steel. The method of annealing recommended is to heat the forgings uniformly at a temperature of 1,425 to 1,475° F., remove them from the furnace and allow them to cool in the air, protected from strong drafts and rain or snow.

TABLE OF TESTS OF SIMPLE CARBON-VANADIUM STEEL.

Analysis: C. 0.47; Mn. 0.90; P. 0.012; S. 0.020; V. 0.15 pct.

Description.	Treatment.	Yield point, lb. per sq. in.	Elastic limit, lb. per sq. in.	Ultimate strength, lb. per sq. in.	Elongation in 2 in., per cent.	Reduction of area, per cent.
7-in. axle	Natural	71,200	68,000	123,000	16.0	30.0
7-in. axle	Annealed 1450° F.	56,000	52,000	90,000	24.0	50.0
7-in. axle	O. Q. 1600; T. 1160° F.	85,000	82,000	112,500	22.0	55.0
11-in. axle	Natural	75,000	70,000	117,000	16.0	28.5
11-in. axle	Annealed 1450° F.	58,000	54,000	94,000	22.0	47.0
11-in. axle	O. Q. 1600; T. 1160° F.	87,000	80,000	115,000	20.5	52.0
Connecting rod	Natural	92,000	85,000	131,000	17.0	44.0
Connecting rod	Annealed 1450° F.	71,500	67,000	105,000	23.5	52.0
Connecting rod	O. Q. 1600; T. 1160° F.	92,500	86,000	123,000	20.5	50.0

Where still higher results are desired than can be obtained by annealing they can be obtained from this carbon-vanadium steel approximating those secured from the more expensive alloy steels. The heat treatment recommended for this is to heat the forgings uniformly to about 1,600° F., and quench in oil. In case water is preferred as a quenching medium, the temperature should be about 1,550° F. The forgings should then be drawn back or tempered by heating to 1,100 to 1,150° F.

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*From The Iron Age.

RADIUM PRODUCTION FROM COLORADO CARNOTITE ORES BY U. S. BUREAU OF MINES.

According to an announcement of Secretary of the Interior Franklin K. Lane the production of radium from Colorado carnotite ores by the Bureau of Mines, in connection with the National Radium Institute, has passed the experimental stage in its new process and is now on a successful manufacturing basis. He also declared that the statements made to Congress concerning the ability of the Bureau of Mines to produce radium at a greatly decreased cost over other processes had actually been accomplished and that the costs were even less than predicted.

The cost of one gram of radium metal produced in the form of bromide during March, April and May of the present year was $36,050. This includes the cost of ore, insurance, repairs, amortization allowance for plant and equipment, cost of Bureau of Mines cooperation, and all expenses incident to the production of high grade radium bromide. When it is considered that radium has been selling for $120,000 and $160,000 a gram, it will be seen just what the Bureau of Mines has accomplished along these lines.

The cost of producing radium in the small experimental plant during the first few months of the Bureau's activities was somewhat higher, but not enough to seriously effect the final average.

The public, however, should not infer that this low cost of production necessarily means an immediate drop in the selling price of radium. The National Radium Institute was fortunate in securing through the Crucible Steel Co. the right to mine ten claims of carnotite ores belonging to them and this was practically the only ore available at the time. Since then new deposits have been opened, but these are closely held and, according to the best judgment of the experts employed by the Bureau of Mines the Colorado and Utah fields, which are much richer in radium bearing ores than any others known, will supply ore for a few years only at the rate of production that obtained when the European war closed down the mines. The demand for radium will also increase rapidly, for the two or three surgeons who have a sufficient amount of this element to entitle them to speak from experience are obtaining results in the cure of cancer that are increasingly encouraging as their knowledge of its application improves. A few more reports like that presented to the American Medical Association at its recent San Francisco meeting and the medical profession as a whole will be convinced of its efficacy. Under all the circumstances that have come to my knowledge it does seem to me that it behooves the Government to make some arrangement whereby these deposits, so unique in their extent and their richness, may be conserved in the truest sense for our people, by extracting the radium from the ores where it now lies useless and putting it to work for the eradication of cancer in the hospitals of the Army and Navy and the Public Health Service.

The ten carnotite claims being operated at Long Park, Colorado, by the National Radium Institute have already produced over 700 tons of ore averaging above 2 per cent uranium oxide. The cost of ore delivered at the radium plant in Denver has averaged $81.30 per ton. This included 15 per cent royalty, salary of Bureau of Mines employes, amortization of camp and equipment and all expenses incident to the mining, transportation, grinding and sampling of the ore.

A concentrating plant for low grade ores has been erected at the mines and is successfully recovering material formerly wasted. Grinding and sampling machinery has been installed at Denver and a radium extraction plant erected in the same city. The radium plant has now a capacity of three tons of ore per day, having been more than doubled in size since last February. Before that time the plant had been run more or less on an experimental scale although regularly producing radium since June, 1914. To July 1, slightly over three grams of radium metal had been obtained in the form of radium barium sulfate containing over one milligram of radium to the kilogram of sulfates. The conversion of the sulfates into chlorides and the purification of the radium therefrom is easily accomplished and with very small loss of material. Unfortunately, however, special acid proof enamel ware, obtainable only in France, has not been delivered of sufficient capacity to handle the crystallization of the full plant production, so that a little less than half the output, or to be exact 1304 milligrams of radium element have been delivered to the two hospitals connected with the National Radium Institute. The radium remaining can be crystallized at any time from neutral solution to apparatus already installed, but the greater rapidity and efficiency of production of this very valuable material by the methods used have decided the Bureau of Mines to await the completion of apparatus now being built before pushing the chloride crystallization to full capacity.

The average radium extraction of all ore mined by the National Radium Institute has been over 85 per cent of the amount present in the ore as determined by actual measurement. The amount present in the ore has been found, in fact, to be essentially the same as the theoretical amount required by the uranium-radium ratio. The extraction figures for the last five carloads of carnotite treated has shown a recovery of over 90 per cent in each case.

A bulletin giving details of mining, concentration and methods of extraction is being prepared by the Bureau of Mines and will be issued early in the fall.

RETORT COKE ONE-THIRD.

The United States Geological Survey's statistics on coke in 1914 show that the total output in the United States was 34,555,914 net tons, valued at $88,334,217. Of this 23,335,971 tons was made in beehive ovens, with an almost total loss of the by-products, and 11,219,943 tons or 32.5 per cent was produced in by-product ovens, with a recovery of over $17,500,000 worth of by-products, or approximately $1.55 for each ton of coke. As over 23,000,000 tons of beehive coke was made in 1914, and as the yield of coal in coke is less in beehive ovens than in by-product ovens, the loss of by-products from coal made into coke in the beehive ovens in 1914 is put at not less than $40,000,000. The slump in copper and other base metal smelting following the declaration of war last August was responsible for a marked decrease in the coke production in the Rocky Mountain States.

Compared with 1913 the decrease in coke output was 11,743,616 tons, or 25 per cent in quantity, and $40,588,056, or 31.5 per cent in value. The beehive and by-product coke did not suffer equally in the decrease, the former falling off 10,248,859 tons, or 30.5 per cent in quantity, and $30,030,371, or 37 per cent in value, as compared with a decrease in by-product coke of 1,494,757 tons, or 11.8 per cent in quantity, and $10,557,685, or 22 per cent, in value.

Three States, Kentucky, Ohio and Washington, showed increases. These increases were all due to the operation of by-product plants, the building of which was begun in 1912 and 1913. At the end of 1914 there were 99,755 ovens in the United States, of which 5,809 were by-product ovens and 93,946 were beehive. Of the by-product ovens 667, or 11.5 per cent, were idle throughout the year, and 44,450, or 47.3 per cent of the beehive ovens were idle. At the end of 1914 there were under constructon 644 new by-product ovens and 605 new beehive ovens. In the year seventy-one by-product ovens were abandoned, all of which it is expected will be replaced by others of the retort or distillation type, and 3,603 beehive ovens were also abandoned.

The following table gives the output of coke in the United States in 1914 by States:

PRODUCTION OF COKE IN THE UNITED STATES IN 1914, BY STATES.

	Net tons.		Net tons.
Alabama	3,084,149	Virginia	780,984
Colorado	666,083	Washington	84,923
Georgia	24,517	West Virginia	1,427,962
Illinois	1,425,168	Maryland	2,222,134
Indiana	2,276,652	Massachusetts	
Kentucky	443,959	Michigan	
New Jersey	255,283	Minnesota	
New Mexico	362,572	Utah	
New York	457,370	Wisconsin	
Ohio	521,638		
Pennsylvania	20,258,393	Total	34,555,914
Tennessee	264,127		

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Borax Production in 1914.

The production of crude borate materials in the United States in 1914 was 62,400 short tons, valued at $1,464,400, as compared with 58,051 tons in 1913, valued at $1,491,530. This is fan increase in quantity of 7½ per cent, according to Charles G. Yale and Hoyt S. Gale, of the United States Geological Survey. All the crude borate material now used in this country is the mineral colemanite. The product during 1914 was obtained from three mines, all in southern and southeastern California, the larger part coming, as usual, from the Lila C mine of the Pacific Coast Borax Co., in the mountains of the Death Valley region of Inyo County. During the year this company completed a calcining plant at Death Valley Junction to roast the lower grade ores before shipping them to New Jersey to be refined. It also completed a narrow-gage railroad from the Tonopah & Tidewater Railroad at Death Valley Junction to the Biddy McCarthy and Monte Blanco mines of the company in the Furnace Creek region, which have not yet been operated.

The Sterling Borax Co., near the border of Los Angeles County, was second in production. Two grades of ore are mined and are roasted to remove impurities. On calcination the colemanite content of the ore is dehydrated and becomes a fine powder.

The Stauffer Chemical Co., of San Francisco, which was once interested in the borax mines at Lang, has obtained a controlling interest in the holdings of the Russell Borate Co. in the Ventura district. This company hauls the ore 35 miles to rail and ships it to San Francisco for refining. The season is limited to about seven months in the year on account of heavy roads in winter.

A 40-foot deposit of colemanite is reported to have been discovered at a depth of 370 feet by ranchmen drilling for water about 4 miles from Rich station in the Kramer district, San Bernardino County, Cal.

Chile and the United States lead the industry with approximately equal output of borates, or boric acid and borax, each producing in round numbers about 40,000 to 50,000 metric tons of crude ores, mainly calcium borates. Turkey probably stands third in rank of production, with a reported average production of 14,000 tons reported as boracite; and Peru, Bolivia, Italy, Argentina, and India are also producers.

The price of borax crystals is quoted as 3¾ to 4 cents a pound, though it rose to 4¼ to 4¾ at the very close of the year. The price of boric acid crystals, which is normally 7 to 7½ cents a pound, advanced to 7¾ to 8½ cents at the close of the year. The tying up of some foreign sources of supply, as, for instance, the mines on the Sea of Marmora, and the interruption of foreign business has created somewhat larger demand for the American products, and a slight rise in price may be expected.

Requirements of Pulp for Viscose.

A practical pulp manufacturer, states the editor of *Paper*, has experienced some difficulty in preparing sulphite cellulose of satisfactory composition for conversion into viscose. He asks whether the wood should be cooked with strong or weak acid, cooked slowly or quickly, and should it be blown off at a very low test—that is, when the acid is practically all exhausted.

We gather from talks with men who have specialized in the manufacture of viscose, that it does not matter much how the wood is cooked, though the best results are obtained with an easy bleaching sulphite by the slow cook process. It should be blown off when titration of the liquor shows the per cent of SO_2 to be about 0.16 or 0.13. The principal thing to guard against is overbleaching and the complete removal of bleach residues must be absolutely assured.

One of the difficulties encountered in the conversion of bleached sulphite of American origin into viscose is the greater quantity of rosin it contains as compared with foreign pulps. It will be understood, therefore, how necessary it is to remove every trace of rosin, as well as bleach, before attempting the manufacture of viscose from bleached sulphite cellulose.

It is understood, of course, that the cellulose will receive a preliminary treatment with a dilute solution of hydrochloric acid. Seidel's process is to treat the sulphite cellulose for a few hours with one per cent of hydrochloric acid in water. The pulp is afterwards squeezed and washed thoroughly, before being brought into contact with a 40 per cent solution of caustic soda in water, where it is kept for three days in a closed container. At the end of that time carbon disulphide is added with constant stirring. The whole is allowed to stand for twelve hours, when the viscose is precipitated either by alcohol or sodium chloride.

American Potash.

The *American Fertilizer* in a recent editorial note comments as follows on the fact that American potash in commercial quantities is in sight. One of the concerns which has been doing extensive research work with Utah alunite for more than two years, is now pushing work on a good-sized plant, and expects to be shipping potash early in the fall. The company has plenty of capital and skilled labor, and have doubtless solved the main problems in the reduction of alunite. We will have no German potash this year, and very likely none next year, so the Utah factory is assured of a ready market for all it can produce at prices far above normal. At least one other company is planning to make alunite potash, and work is well advanced on the very large operation at Searles Lake, in Southern California, which will produce several chemicals, potash being among the number. The Government chemists still insist that kelp furnishes the most promising source of supply for potash. A good deal of experimental work has been done on kelp by several concerns, without much financial success. There seems to be that wide gap between theory and practice which is found so often in new undertakings. The makers of American potash will have some hard problems to solve, but we learn by doing. American chemists have worked miracles in other lines. We believe they will be equally successful with potash.

In connection with these developments it is interesting to note that interests associated with Armour & Co. have embarked on a new enterprise involving the production of potash in the United States on a commercial scale for the first time. Charles H. MacDowell, president of the Armour fertilizer works, is vice-president of the corporation formed to develop the project the name of which is the Mineral Products Company. The new corporation is not owned by Armour & Co. but by persons associated with the Armour organization and the General Chemical Company. The Mineral Products Company, it has been announced, will erect a large plant in Utah for the extraction of potash from alunite by a process for which the company owns the patent. The following outline of the project is taken from a letter from Mr. MacDowell to the editor of the Chicago *Chemical Bulletin*.

The alunite property in South Utah known as the Custer Claims and described in Bulletin 511, United States Geological Survey, is to be developed by the Mineral Products Corporation. A plant is being installed under the direction of Messrs. Westinghouse, Church, Kerr and Company. The first unit will handle from 100 to 150 tons of ore a day and will turn out approximately from 20 to 30 tons of sulphate of potash. The installation is a rush one and is intended for the time to produce potash but not the other values in the ore. This manufacture will be taken up later.

The Cement Industry Improving.

The year 1915 opened with decidedly slack conditions in the cement industry, the latter part of 1914 having shown a large falling off in production and a still larger reduction in shipments of Portland cement than the corresponding period of the preceding year, as reported by E. F. Burchard, of the United States Geological Survey, and the net result for 1914 was a slight decrease in both production and shipments the first yet recorded. The average price at the mills also decreased.

At the beginning of 1915 there was little new construction work in sight, few cement manufacturers felt optimistic concerning the outlook and some even prophesied a further decline in volume of business for 1915.

The general developments of the early months of 1915 were not such as to dispel the glooms from all of their lodging places, so that the rate of production of many mills was cut down below that of shipments in order to effect a partial clearance of the large stocks that had accumulated during 1914. In general, however, there has been an improvement during the second quarter of 1915, the rate of production of Portland cement having gradually increased, and although there are no statistics available for the first half year it is believed that, as compared with the corresponding period of 1914, no appreciable gain or loss has occurred. If this be true, then conditions really are better than were anticipated by the majority of producers at the beginning of the year, and, if no unforeseen conditions arise seriously to affect business, the next six months should show an improvement over the first half of the year.

The cement industry is particularly subject to local conditions, especially in inland districts, since cement is too bulky a product to be shipped in great quantities by rail into competitive territory, except under extraordinary circumstances. Naturally, therefore, certain districts, such as those that produce cotton, and those in which industrial agitation has recently checked progress, have felt the depression more keenly than the average localities.

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"RELATIVE STABILITIES" IN POLLUTED WATERS CARRYING COLLOIDS.[*]

By ARTHUR LEDERER[†]

As a rule, all river waters contain more or less colloidal matter in the form of very finely divided silt. Polluted waters also carry colloids of sewage origin mainly derived from the fecal matter.

Only recently has the importance of colloids been recognized in sewage disposal and water purification. We know that the colloidal matter in sewage affects the putrescibility of the liquid more than the heavier coarse suspended matter. The removal of the colloids by simple filtration—not biologic filtration—results in an improvement which is, however, much less than the one effected by biologic treatment[1] but far more than by settling. The study of colloids has given the science of chemistry a new aspect. Colloidal chemistry has explained some phenomena in nature as well as technology, heretofore not clearly understood. We differentiate between crystalloidal and colloidal state of matter. A very large number of inorganic substances, heretofore known only in the crystalloidal state, have been prepared in the colloidal. Some substances such as proteins, starch, gum, and glue are known in the colloidal form only. Suspensions of colloidal clay remain suspended in the water for days and weeks. The addition of electrolytes such as common salt, sodium sulphate, calcium sulphate, or sodium nitrate, accelerates sedimentation. The reason for this is (1) the electrostatic attraction between the colloids and the ions carrying the opposite electrical charge: (2) the removal of the water of the colloid. Hygroscopic electrolytes are, therefore, particularly efficient. Colloidal clay adsorbs aniline dyes such as methylene blue. By adsorption we understand the concentration of a dissolved salt on a surface due to difference in surface tension or electric potential. Clays also adsorb and retain other substances such as oils, fats, starch, proteins, certain inorganic dyes, all aniline and plant coloring matter, urine and fecal matter, putrid odors, and a large number of other substances. This property of adsorption has led Professor Rohland of Germany to develop his clay treatment of sewage and industrial waste waters. Adsorption is selective. An interesting study on this point has recently been made by Parker.[2]

When applying methylene blue to waters carrying colloidal suspensions of clay, the dye is adsorbed by the clay and sedimentation occurs, leaving the liquid colorless. The sediment is blue. This adsorption may be only partial; it may take place quickly or slowly, all depending upon the quantity and the character of the colloidal matter present. The adsorption interferes seriously with the quantitative determination desired on the degree of putrescibility of the liquid. In other words, "relative stabilities" obtained in such waters by the methylene blue method cannot be correct. Spitta and Weldert in their original communication[3] advise the observation of decolorization of the sediment after adsorption takes place, though their observations are more of a qualitative nature and in such cases the exact time element is of less importance. In obtaining Phelps' "relative stabilities," the time element is all-important.

Until recently the writer disregarded the decolorization of the liquid in polluted river waters, and accepted the decolorization of the sediment as the criterion. Correspondence between the writer and Dr. F. E. Hale of the Mount Prospect laboratory, Brooklyn, N. Y., developed a difference of opinion regarding the reliability of this procedure. Doctor Hale held that the methylene blue once thrown out of solution is probably inert, and that, therefore, the decolorization of the liquid should be accepted as the sole index of the putrescibility. Doctor Hale's procedure consists in adding one c.c. of methylene green solution at the beginning and continuously thereafter as demanded by adsorption until a slight color persists in the liquid. Decolorization of this was taken as the endpoint. Dr. Hale considers that this method gives good relative results, but probably does not represent absolute values. My aim was to obtain correct relative stabilities, while Dr. Hale's procedure aimed at relative results. In this respect our problem differed. Notwithstanding, I decided to investigate whether the observation of the decolorization of the sediment actually furnishes correct relative stabilities, and if not, which procedure would have to be followed. Jackson and Horton[4] recommend the use of as little methylene blue as possible, on account of its antiseptic properties, and the writer[5] in investigating the quantities recommended in the "Standard Methods" fixed the amount at 0.4 c.c. of a 0.05 per cent aqueous solution per 150 c.c. bottle capacity. When working with waters carrying colloids, it is clear, of course, that there should always be 0.4 c.c. or less of the coloring matter in solution, provided the sediment containing the precipitated coloring matter is actually inert. An excess of coloring matter in solution would interfere with obtaining correct results. If the coloring matter in the sediment retains its antiseptic qualities, even though to a lesser degree, it would still be impossible to obtain correct figures. The entire question depends, of course, upon the value of all methylene blue or other similar "relative stabilities" when applied to liquids other than sprinkling filter effluents.

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[*] Read before the Laboratory Section American Public Health Association, Jacksonville, Fla., December, 1914.

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[1] Lederer, Am. J. Pub. Health, Feb., 1912.

[2] Parker, J. Ind. Eng. Chem., Oct., 1914, p. 831.

[3] Spitta and Weldert; Mitt. kgl. Prüfungsanst. Wasserversorgung, Heft 6, p. 160.

Since the decolorization of the blue color coincides fairly closely with the elimination of the total available oxygen, I first determined the oxygen at the time of decolorization of the liquid and sediment as well. An artificial turbidity of 100 was imparted to a putrescible sewage-water mixture and a number of glass stoppered bottles were filled with this liquid. A number of these bottles were colored in the proper proportion with methylene blue, the others remained as "blanks" for the determination of the residual available oxygen. The results are given in the following Table I.

These tabulated results indicate the following conclusions: A very serious mistake can be made by assuming that the decolorization of the sediment in silt-bearing waters is the correct measure of the "relative stability." Experiments 3, 4, 5, 6 and 7 show that the decolorization lags far behind the elimination of the available oxygen in such liquids or in other words the methylene blue, once adsorbed, is largely inert as an indicator. This bears out Dr. Hale's assumption. The adsorbed liquid is, however, not entirely inert, as otherwise the sediment would never decolorize. The fact that the sediment decolorizes only under prolonged ultra-anærobic conditions makes such an observation useless for quantitative purposes. Reliance on the decolorization of the liquid is equally doubtful because we cannot tell to what extent the decolorization is really adsorption. We can only be fairly certain of obtaining accurate "relative stabilities" if we knew that 0.4 c.c. or less of the coloring matter per 150 c.c. bottle capacity would remain in excess over the adsorption requirements, and that the adsorbed methylene blue was entirely inert. This cannot be insured under practical conditions, but remains a matter of chance. If more than 0.4 c.c. of the coloring matter remains in solution, the antiseptic qualities of the dye would make itself felt and higher "relative stabili-

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[4] Jackson and Horton, J. Ind. Eng. Chem., Vol 1, June, 1909.
[5] Lederer, Am. Jour. Pub. Health, Vol. 4, p. 241.

TABLE I.—ELIMINATION OF AVAILABLE OXYGEN IN TURBID WATERS ON APPLYING THE METHYLENE BLUE PUTRESCIBILITY TEST.

Serial No.	Date and Time 1914	No. of cc. 0.05 pct. methy. blue added per 150 cc. capacity.	Color of supernatant liquid in 24 hours.	Time of decolorization of liquid in hours.	Time of decolorization of sediment in hours.	P. P. M. total initial available oxygen.	P. P. M. residual oxygen at time of decol. of liquid.
1	April 14 11:00 a. m.	0.4	colorless	24	Sediment did not decolorize in 10 days	23.3	10.5
		0.8	colorless	24		23.3	10.5
		1.2	colorless	24		23.3	...
		2.0	blue	blue after 10 days		23.3	...
2	April 15 10:30 a. m.	0.4	colorless	24	Sediment did not decolorize in 10 days	23.5	8.8
		0.8	colorless	24		23.5	8.8
		1.2	colorless	24		23.5	8.8
		2.0	blue	blue after 10 days		23.5	...
3	April 20 11:00 a. m.	0.4	colorless	20*	88	20.1	0.5
		0.8	colorless	20*	105	20.1	0.5
		1.2	colorless	20*	112	20.1	0.5
		2.0	slightly blue	45	119	20.1	0.4
4	April 23 11:00 a. m.	0.4	colorless	21	Sediment did not decolorize in 10 days	22.1	4.7
		0.8	colorless	24		22.1	4.7
		1.2 }	slightly blue	48		22.1	0.6
		2.0 }		93		22.1	0.5
5	April 27 11:00 a. m.	0.4	colorless	20*	52	18.7	0.5
		0.8	colorless	20*	61	18.7	0.5
		1.2	colorless	20*	70	18.7	0.5
		2.0	blue	45	76	18.7	0.4
6	April 29 11:00 a. m.	0.4	colorless	20	100	21.0	2.9
		0.8	colorless	20	118	21.0	2.9
		1.2	colorless	20	127	21.0	2.9
		2.0	blue	45	142	21.0	0.7

*Decolorized during the night, therefore estimated but roughly. The absence of the residual oxygen at the time of the decolorization of the liquid is of course due to the fact that the oxygen has not been determined at the exact time of decolorization.

ties" would result. The adsorption of the coloring matter seems to bear a definite relation to the amount of colloidal matter present, and indeed some German observers have recommended a quantitative procedure for determining colloids on this basis. The methylene blue test in waters carrying colloids is, therefore, of negative value only; *i. e.*, if the blue color of the liquid persists irrespective of adsorption, the "relative stability" is 100, or an excess of oxygen may be present.

A number of coagulants, such as freshly precipitated aluminum hydrate, magnesium hydrate, calcium carbonate and calcium oxide were employed to mechanically settle the colloids previous to introducing the coloring matter. The results were not sufficiently encouraging to follow this line of experiment. The addition of electrolytes to sewage, such as common salt, did not accelerate the sedimentation sufficiently to be of practical advantage.

I am forced to conclude that it is useless to determine "relative stabilities" in turbid waters by the methylene blue method. This is unfortunate, since it robs us of a simple and convenient field procedure. To obtain the correct oxygen demand in such waters, the following procedure is requisite:

Determining the initial available oxygen. The free oxygen has to be determined on the spot. A sample for nitrate and nitrate determination can be preserved with chloroform and shipped to the laboratory. Three other samples should be collected carefully to avoid aeration. To one sample add either a certain quantity of fresh water (free of nitrites and nitrates) with a known oxygen content or a definite quantity of saltpeter.[6] Personally, I prefer to add saltpeter, since it is a much simpler procedure. The other two samples remain as originally collected. All of these samples are now incubated in closed bottles for ten days at 20° C. At the end of this incubation period, the residual available oxygen is determined in the samples devoid of saltpeter or additional water. The other sample is examined quantitatively for nitrites and nitrates. If free oxygen remains at the end of incubation the residual saltpeter oxygen need not be determined. All figures are referred to one liter of original river water. The nitrite nitrogen multiplied by 1.7 and the nitrate nitrogen multiplied by 2.9 express equivalents of oxygen. The initial available oxygen minus the residual oxygen expresses the biochemical oxygen demand. When the water is very badly polluted, the free oxygen sample need not be incubated for the reason that the free oxygen is certain to be absent after incubation. In connection with these incubations, it is important to keep in mind that the nitrites and nitrates are attacked while free oxygen is still present. As a rule, the nitrites and nitrates begin to be attacked when the free oxygen content is reduced by about 50 per cent.

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[6] Lederer, J. Infect. Dis., Vol. 14, p. 482.

GOVERNMENT INQUIRY INTO SHORTAGE OF DYES.*

The shortage of dyestuffs in this country has reached such an acute stage that the Federal Government has decided to take a hand in the situation with a view to developing all the facts brought about by the shutting off of German colors and intermediaries, and then determining what measures of relief, if any, can be obtained with the least delay.

As long ago as last January conditions began to be alarming, notwithstanding the fact that several special shiploads of colors were brought here direct from Bremen and Rotterdam. The United States Senate adopted a resolution last winter calling upon Secretary Redfield of the Department of Commerce for a report covering the then prevailing situation. Dr. E. E. Pratt, chief of the Bureau of Foreign and Domestice Commerce, picked Commercial Agent Thomas H. Norton to make the investigation.

Toward the close of March, the agent presented a comprehensive report dealing with the nature of the dyestuffs used by American industries, the sources of supply, and bringing into high relief the predominance of Germany in the field of color production. The limited extent of the American dyestuffs industry was also emphasized. All factors connected with the creation of a self-contained, independent, domestic coal-tar chemical industry were given in full in the report, together with the problems involved by a cessation of the usual foreign supplies.

Since the filing of that report all signs have pointed to an increasing serious menace to the steady operation of domestic industries unless some means were found to bring in additional supplies. While American color plants established before the war have gone to work energetically to help supply the wants of industries, it has become apparent that their efforts will not be sufficient for months to come. Other concerns starting after the war are now beginning the production of intermediates or chemicals, while few are understood to have made much progress in turning out the wanted dyestuffs.

Latterly, textile, leather, and other manufacturers have informed Secretary Redfield that, unless something drastic is done at once, industries must close in whole or in part, depending on circumstances. The secretary, after consultation with Dr. Pratt, has decided to get the ideas of manufacturers in all lines concerning what should be done to remedy the situation. With this in view, Commercial Agent Norton has been ordered to this city for the purpose of conducting an exhaustive new investigation into the dyestuff situation as it has developed up to this time.

Dr. Norton has established a bureau in the Custom House, New York, making Room 525 his headquarters. His chief assistant is Dr. J. M. Langdon, a graduate of the University of Munich, formerly an assistant professor of chemistry at the University of Heidelberg, an expert in manufacturing aniline dyes. It is their purpose to stimulate the use of now wasted by-products capable of forming the basis for dyestuffs. They desire that these manufacturers and men with capital consult with them. The bureau will be maintained at least two months.

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*From Paper.

"We propose to go into all industries which may be benefited by the department," said Dr. Norton, "but we shall devote ourselves principally to the chemical industry. On account of the shortage of chemicals, nearly every industry in the country is deprived of something necessary or desirable.

"This condition exists in a country with raw material to supply all the needed products, with plenty of capital and with abundant business initiative. We need to co-ordinate the forces of American resources, American brains and American capital. Among the thousands of chemists and graduates of our technical schools we are looking for a dormant chemical Carnegie to do for the American chemical industry what Carnegie and Edison did for the steel and electrical industries.

"Dyestuffs and potash are the most important materials which the war has shut off. We have depended on Europe for nearly all our dyestuffs and on Germany for all our potash.

"There is no reason why this condition should continue. Our coke industry wastes about $100,000,000 a year in by-products which form the crude material for aniline dyes. The Germans utilize every ounce of these products. We utilize only 16 per cent of those gases from which may be taken such hydrocarbons as benzol, toluol, benzine and carbolic acid.

"These are the raw materials for high explosives, as well as for aniline dyes, and their high price, due to the demand from manufacturers of explosives, adds a difficulty to the infant dye industry. Yet the prices of dyestuffs are high and should encourage investment of capital. The textile industry of the country uses $100,000,000 of materials yearly, and though only one or two per cent is dyestuffs, that percentage is essential to trade.

"We now import $97,000,000 of chemicals a year and export $27,000,000. We want to reverse these figures. We don't want to send crude material abroad and buy it back in the manufactured form.

"There is no end to the chemicals which we now import at the rate of $200,000 to $40,000,000 a year. There is oxalic acid, of which we bring in $400,000 worth. It is made from sawdust and caustic soda. We have the soda and in the northwest there are nonproductive sawdust piles without number.

"We import $600,000 worth of casein for the use of paper manufacturers. That imported casein comes from Danish cows. Why not make it from our own cows?

"Every little village has a photographer who is short of developers. We can make the photographic developers for him. They are coal tar products. There are scores of such problems that we can solve if we set our minds to it."

Questioned in regard to the objection that the American manufacturers could not compete with the Germans after the war. Dr. Norton replied that a protective tariff of 30 per cent now lessened the chance of such injury to a growing industry. What might be most desirable in this connection, he thought, was an anti-dumping law protecting the home markets from the danger of the dumping of an excess of German dyestuffs at slaughter prices.

THE ELECTROCHEMICAL POSSIBILITIES OF THE PACIFIC COAST.*

By J. W. BECKMAN.†

AVAILABLE POWER.

Potential Water Power on Pacific Coast.—Forty-three per cent of the potential water power of the United States is to be found in the comparatively narrow strip of land bounded by the Rocky Mountains and the Sierras in the East, the Pacific Ocean on the West, by Canada in the North and Mexico in the South.

The U. S. Government gives the minimum potential water power in the whole of the United States as 26,736,000 h. p. Of this, 11,504,000 h. p. is available in the States of Washington, Oregon and California, divided up between them as follows:

	H. P.
Washington	4,932,000
Oregon	3,148,000
California	3,424,000

Developed Water Power on Pacific Coast.—According to figures compiled by Mr. W. E. Herring, of the Puget Sound Traction, Light & Power Company, it is evident that only a very small per cent of the power available in these States is developed. The following figures show the distribution of developed power:

	Developed H. P.	Percent of Possible Power
Washington	306,000	6
Oregon	105,000	3
California	430,000	8

Power in Alaska.—Alaska belongs to the west coast of the United States. The potential water powers of Alaska have never been estimated, but conditions in the southeastern section of the territory especially are such that they promise in a way to rival Norway, as to cheap and abundant water power. So far only a very small fraction of the available powers has been developed.

COST OF ELECTRIC POWER.

The cost of electric power on the Pacific Coast has often erroneously been thought prohibitive for electrochemical industries.

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*Paper presented at the 28th general meeting of the American Electrochemical Society in San Francisco, at a joint session with the American Institute of Electrical Engineers, Sept. 17, 1915.

†Chemical Engineer, Great Western Power Co.

Cheap Power.—Power can be obtained close to the generating stations as cheap, if not cheaper, than the prices generally quoted for power at Niagara Falls.

"Off-Peak" Power.—Of course, the power at the end of a long transmission line is considerably higher priced than close to the generating station, but even so, if the industries can operate on so-called "off-peak" power at such a point, big reductions are offered the consumer. The size of this reduction depends on the consumption, and may even amount to 40 per cent of the prevailing price.

Great Western Power Co.—The Great Western Power Co., which operates the largest power house on the Pacific Coast, is able to furnish power, if sufficiently large blocks are desired, at such prices that even the fixation of atmospheric nitrogen carefully conducted would be a financial success.

The power house and power sites of this company, from which close to 600,000 h. p. can be developed in large blocks, are all located within easy reach of tidewater. As a comparison, attention is drawn to the fact that Niagara Falls is four times as distant from tidewater as the above mentioned power sites.

Besides proximity to tidewater, this power is favored by being surrounded with various raw materials essential to electrochemical and electrometallurgical operations. For these reasons this power is perhaps best fitted as a prime mover in the electrochemical development of the Pacific Coast.

If it is further realized that one-fifth of all the population of the Pacific Coast resides around the San Francisco Bay, it is plain that this Company, which supplies this section with power, holds a key to the immediate electrochemical development of this part of the United States.

Speel River, Alaska.—There are, however, a number of other power projects which will be able to furnish power cheap enough to compete with the proverbially cheap power of Norway. Such power can be obtained in Alaska at the well-known project on Speel River, ideally located on tidewater.

The Dalles, Oregon.—Another project is that at The Dalles, Oregon, on the Columbia River, close to the newly-opened Celilo canal, which makes the whole of Columbia River navigable.

Undeveloped Power.—All through this section of the United States there is still a great deal of water power, the development of which is not yet even projected, and many of the sites are so located that their development would be exceedingly cheap; but on account of somewhat remote location, scarcity of population and lack of electrochemical enterprise, they might be failures if developed at the present time.

LABOR.

In a way it is a futile thing to formulate opinion as to labor and its conditions on the Pacific Coast while this terrific struggle is going on in Europe, where thousands of men, if not millions, are being permanently taken out of the labor market. But in spite of this, it is problematical whether the opening of the Panama Canal will have a marked influence on the labor market of the Pacific Coast.

Nationality of Labor.—It is significant of the labor on this coast that it is composed practically exclusively of either native-born Americans, or of foreign-born Americans who have to a great extent lost touch with the European country from which they originally hailed.

Exceptions to this are naturally the Orientals and Hindus, who seem to devote the greater part of their activity to agricultural and logging occupations, and as is well known they are not met on the Pacific Coast, justly or unjustly, with a "welcome." Through international "gentlemen's agreements," and through exclusion, the inflow of this type of labor has to a great extent been limited, if not eliminated.

The labor, therefore, that has to be counted with at present is really the best type of European—the man who is familiar with both the language and the ways of the land, the man who is wide-awake among his own countrymen and has been able to shake the shackles of the congested foreign sections of the large Eastern cities, the squalor of its mining and manufacturing towns, and, escaping the padrone, has taken his destiny in his own hand.

It can, from this, be understood that industries operating on the Pacific Coast get the pick of the Eastern labor market.

Direct Importation of Labor.—For a long time much the same conditions will prevail. Since European laborers are gregarious, they go only to centers already established by their own countrymen, and from such a point they branch off.

Only when a large population of directly imported foreign European labor has collected in Pacific Coast centers, due to industrial advantages, will there be a direct influx of European labor of any magnitude to the Pacific Coast.

Cost of Labor.—The cost of labor does not differ very materially on the Pacific Coast from that prevailing in Chicago. An extensive investigation has been made of prevailing labor prices, and the following figures are the result:

	Per day.
Unskilled labor	$1.50 to $3.00
Skilled labor	3.00 to 3.50

The average working day is eight hours.

Labor and Climate.—The climate of the Pacific Coast should not be overlooked in considering labor conditions and labor costs. With the modern researches made into efficiency and the effect of climate on same, it is well to appreciate that the equitable climate of the Pacific Coast, with mild winters and cool summers, is very stimulating and the average annual output of a laborer is materially greater on the coast than in the East.

Trade Unions.—Labor is fairly strongly unionized in some sections of the coastal states, while in others the open shop prevails.

RAW MATERIALS.

Refractories.—Magnesite: Considerable has been said recently about California magnesite, and too much cannot be said about it, since the California magnesite is extremely refractory, being practically pure magnesium carbonate. With suitable admixtures it should furnish an ideal material for furnace linings.

There are large deposits of this mineral in California, and so far these deposits have not been extensively worked.

Asbestos: Short as well as long fibred varieties are to be found in large quantities in California and other localities of the Pacific Coast.

Kieselguhr: Large deposits are found, of such nature that solid blocks can be cut out and used in furnaces and other constructions.

Fire Clay: Very high quality is being dug, and excellent fire brick are being produced on the Pacific Coast. The bricks have been giving better results in open-hearth operations here than the best standard fire bricks of the East.

Dolomite: Good and extensive deposits are found at various points on the Pacific Coast.

Quartz: Quantities of pure quartz deposits are available, in rock formation as well as sand.

Most of the materials mentioned above occur in various quite widely distributed points on the Pacific Coast, and mostly in easy reach of transportation.

Reducing Materials.

Anthracite: The Pacific Coast is not favored in the same manner as the East with high-grade anthracite coals, at least not at present. Alaska is as yet only a potential producer of coal, but this territory promises to supply the west coast in the near future with high grade anthracite coal, low in ash and sulphur.

Soft Coal: Alaska, British Columbia, and the State of Washington are all producers of soft coal, and at various places on the coast lignites are located. These coals do not have any value at present, except for ordinary purposes.

China, Japan and Australia all supply the coast with coal, some of which is high-grade anthracite of quality and at prices which make it possible for them to compete advantageously with coal brought in from the East.

Charcoal: Many of the densely wooded districts of the Pacific Coast have great abundance of timber, which in many cases would really be improved if part of it were carefully cut, and burnt into charcoal.

Southeastern Alaska especially is covered by overgrown timber, ideal for charcoal burning. It is obtainable practically at no cost whatever, and the charcoal would provide a pure carbonaceous material, comparatively cheap, for reducing purposes.

Natural Gas: The enormous oil fields of the southern part of California furnish in many cases, besides oil, great quantities of gas, an ideal reducing material in metallurgical processes.

Oil: Present in great abundance, much of it practically free from sulphur. It offers in itself all the essentials for reducing metals from their ores.

Present day technique has as yet not evolved ways and means by which the two latter reducing agents can be used with success in electrometallurgical processes, but since the essentials necessary in reducing exist in natural gas and oil, it is purely a question of application of thermal and mechanical details to make such processes operative.

Lampblack: As coke is obtained as a by-product in the manufacture of illuminating gas from soft coal, so a very fine lampblack is produced in gas plants operating with crude oil. The lampblack formed is practically pure carbon, except for a small amount of heavy oil mixed in with it. A considerable quantity of this material is produced every day at the various gas houses along the coast, and forms an ideal reducing material, since it contains no ash and no sulphur. At present this material is a by-product, and offers in many cases the problem of how to most advantageously dispose of it.

On account of its physical condition and its purity it offers an ideal raw material for the manufacture of carbon electrodes, for which there already is a demand on the coast, and this demand is bound to grow rapidly from now on.

Fluxing Materials.

Limestone: Large and conveniently located deposits of limestone of high degree of purity are to be found at many and varied locations on the Pacific Coast, offering ample, cheap and certain supply of this important mineral. With the cheap fuel available, burnt lime can be produced to advantage at about $3.00 per ton.

Salts: Especially in the arid regions of southern part of California, in the deserts, there are large deposits of various salts. Sodium sulphate, sodium carbonate, sodium chloride, and sodium nitrate are all found. Sodium chloride is also obtainable very cheaply along the beaches of the Pacific Coast. The salt ocean water is evaporated in shallow basins by means of sun and wind, and deposits are formed of practically pure salt, suitable for industrial or domestic purposes. This salt can be produced and stacked ready for transportation for about $1.50 per ton.

What promises to be of interest not only to the electrochemical industries but also to the world at large is the occurrence of considerable quantities of potassium chloride in the southern part of California. These deposits are being developed and will shortly be a source of potash to be considered for more than one purpose.

The increasing demand for boron and its compounds can be filled from the large borax deposits in the Pacific Coast States.

Metalliferous Raw Materials.

Iron Ores: That the Pacific Coast holds some unusual iron ore deposits, unusual both as to size and quality, is not always realized. The quality of some of the ore is such that it can compete with some of the best Swedish ores. There is no reason why the Pacific Coast, with abundant supply of high grade iron ores, quantities of cheap oil and charcoal, and hydro-electric power obtainable in great quantities at low prices, should not be an iron producing section of the world, the products of which would figure largely on the world's markets. The time is not distant when such will be the case.

All the necessities for an extensive steel industry are to be found in the shape of ores suitable for the manufacture of alloys such as ferro-manganese, ferrochromium, ferro-vanadium, ferro-silicon, ferro-tungsten, ferro-molybdenum and others.

Barium, both in the shape of sulphate and as carbonate, is to be found in large deposits and in accessible localities.

Bauxite, suitable as raw material for aluminum manufacture, can be found; so also the tin ore *Cassiterite.*

Zinc occurs abundantly; in many mine operators' opinions too abundantly in connection with copper ores, and the mining world is eagerly waiting for some commercial process to treat copper ores containing considerable amount of zinc, recovering both the copper and zinc.

Copper occurs in great quantities, and in lesser quantities *lead, silver, nickel, mercury* and *uranium. Gold* and *platinum*, occurring only in native condition, are of no special interest in this connection.

In making mention of these various metals, it is with the intention of showing the multitude of possibilities open to the electrochemist and electrometallurgist, and although many of these metals are at present obtained from ores found on the Pacific Coast, by means of operations more or less costly, there still remain possibilities where these methods can be substituted both economically and efficiently by utilizing new forces and new agents.

POSSIBLE INDUSTRIES.

From the foregoing it is apparent that there are a great number of industrial possibilities here, but there are a few that are perhaps more apparent than others.

Caustic Soda and Bleaching Powder.—The industry most promising at the present time, for an early development, is the manufacture of caustic soda and bleaching powder. This industry and its possibilities have been thoroughly investigated, and it is established that a medium-sized caustic acid plant could be operated not only successfully but very profitably on the Pacific Coast.

Potassium Chlorate.—Potassium chlorate manufacture is another industry which should have special possibilities here, with the raw materials necessary for it produced on this coast.

Calcium Carbide.—The demand for calcium carbide in South America is great, and also in the mining districts of the western part of United States. The raw materials are obtainable here and the manufacture of carbide should become a flourishing industry on the coast.

Nitrogen Fixation.—Nitrogen fixation industries seek very cheap power, and such power is available here, as well as a very large market for the product. The soil of the costal region is getting quickly depleted of nitrogen, while in some sections the soil is physically well adapted for farming purposes but lacks notrogen altogether. Artificial fertilizer is therefore a great and urgent need for this part of United States.

Iron and Steel.—This industry, as has been indicated before, has great possibilities on the coast, and although the present electric shaft furnace plant in Northern California has not been a total success, there is every reason to believe that success would be won if past experience as well as present practice in Sweden were utilized, together with the application of new principles using oil, or oil and charcoal, as reducing agents.

The demand for high-grade steel castings, produced by means of the electric furnace, is large here, and although there are now three small furnaces operating on the coast there is place for a number of others.

Cyanide.—The Pacific Coast should logically be the world's distributing center for cyanide used in gold extraction. With raw materials suitable for the manufacture of this salt available, electric power, and the market all close at hand, such an industry should flourish.

Aluminum, Lead, Zinc, Copper.—Aluminum manufacture, lead reduction, zinc production, and the electrolytic refining of copper are other electrochemical industries which should be developed on the Pacific Coast. Practically all of the blister copper produced here is shipped east for final refining, when in reality conditions are perhaps even more favorable for this process on the Pacific Coast, where the metal is produced, than in the east.

MARKETS.

Sweden and Norway are looked upon as the world's electrochemical countries *par excellence*. Cheap water power has been held up as one of the reasons of this position, and it is worth noting that if Sweden and Norway had as many opportunities for large, cheap power installations as there are on the Pacific Coast, these countries would dominate the world with their electrochemical products. But the electrochemical industries there would be total failures, even if the processes were working to a nicety, if they had no market for their products.

The total population of those two countries amounts to 10,000,000 people, which to a great extent have agriculture or fishing as their occupation, thus furnishing only limited domestic market possibilities. Still, the industries there are successes in spite of limited home markets, because they have looked to markets beyond the boundaries of their countries, entered the world markets and there found outlets for their products. These markets are free and open to each progressive nation or individual.

Pacific Markets.—Electrochemical industries on this coast have to be inspired with the same desire as those in Sweden and Norway, since the population of the Pacific is about 5,000,000 people. With more than half the world's population dwelling in lands facing the Pacific Coast, these markets are just waiting to be taken by industries located on this coast.

It may justly be said that the greater part of these countries facing the Pacific Coast are populated by people that are still living under primitive conditions, and their demands are limited. Such assumption may be partly correct today, but earlier experiences show that as these countries get more and more in touch with the well organized nations of the world, their needs for the products of these nations increase correspondingly.

This fact is startlingly apparent from statistics obtainable from the Philippine Islands, showing the imports prior to American occupation of the Islands in 1899 and after.

Figures received from the War Department's Bureau of Insular Affairs show that imports have more than quadrupled during the fifteen years the Philippine Islands have been under U. S. control, while they were practically stationary during the six years prior to U. S. occupation. The increase is quite significant, indicating the growth of imports as a country gets in touch with more modern conditions.

Many of the South American and far eastern markets are now open, leaving unprecedented commercial opportunities for industries located on the Pacific Coast.

FINANCIAL CONDITIONS.

There was a time in the history of the Pacific Coast when gold mines and oil wells were the only undertakings which would interest men with capital. Fortunes were made and lost over night. The Pacific Coast is outgrowing this neurotic condition.

Men with money are still eager to make more, but wild, sky-high flights in the financial world have lost their interest; financiers are as conservative on the Pacific Coast as they are in New York City.

It is natural for the West to look east for capital, but it is also equally natural for the West to look inside of its own boundaries for capital. The time is not far distant when financially the Pacific Coast, although not emancipated from the East, since this is impossible, will walk side by side with New York and other Eastern money centers, equally prepared to take as well as to give assistance in the realm of finance.

CONCLUSIONS.

The Pacific Coast is still practically an untried country from the electrochemist's point of view. Enormous quantities of cheap, undeveloped power are still to be found, and developed power is available at prices such as rival the cheapest water power of the East. The natural resources of the costal districts are unlimited. They abound in minerals suitable for refractories and fluxing.

Charcoal, oil, natural gas, and lampblack from gas houses, as well as high grade anthracite, suitable for reducing purposes, are all obtainable on the Pacific Coast.

A great abundance of various kinds of salts and metalliferous ores are present in diverse localities of the Pacific Coast, offering unusual opportunities for electrochemical and electrometallurgical industries.

Conditions on the Pacific Coast are now ripe for various electrochemical and electrometallurgical undertakings. The manufacture of caustic coda is especially well adapted to this section; low salt cost, low fuel cost, cheap power and large market for the caustic as well as for the bleach assures immediate success to such an undertaking.

The labor obtainable is the very best, and is not higher in price than in Eastern centers.

The climate is ideal.

The financial conditions of the Pacific Coast are sound. "Blue-sky" laws protect the investor against wildcat schemes.

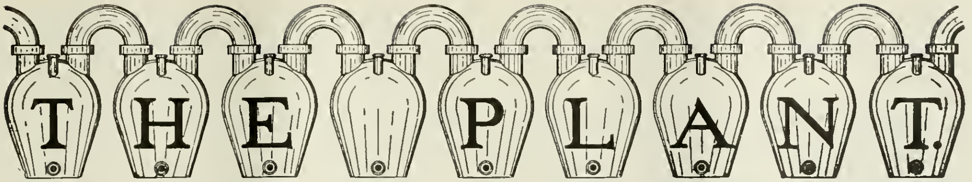
Any industry operating on the coast would have to look to other markets than the local ones for its products. With more than half of the world's population facing the Pacific Coast, an industry here has greater commercial possibilities and opportunities than one located in Sweden or Norway, which have large nearby, fully developed markets, but also keen competition to contend with.

But for a few small electrochemical industries on the coast, electrochemistry would be unknown here, excepting by its name. The Pacific Coast has as yet not financial strength, nor experiences enough, to build up these industries alone.

The possibilities are here; the Pacific Coast is quickly waking up to this fact, but is forced yet for some time to look east for its electrochemical stimulus.

Will the east come west and give it?

Cotton mills in India produced 181,000,000 lbs. of yarn during the three months, April to June, 1915, compared with 174,000,000 lbs. in the 1914 period and 169,000,000 lbs. in the 1913 period. Woven goods manufactured totaled 82,000,000 lbs. in April-June, 1915, compared with 69,000,000 lbs. and 66,000,000 lbs. in the correspondinng quarters of 1914 and 1913. Most of the yarn spun runs below 26s.



THE PLANT.

THE MANUFACTURE AND USES OF WROUGHT MANGANESE BRONZE.*

By JESSE L. JONES.

Manganese bronze when introduced into the United States from England about 1893, found its first important application in the manufacture of propeller blades because of its strength and toughness and the fact that it is practically incorrodible in sea water.

The low melting point of the cast manganese bronze and the ease with which it can be cast into the most intricate forms lead to its adoption for many automobile parts and numerous other applications where service conditions are extremely severe.

The rolling and forging grades of manganese bronze had at first very few applications. The greater cheapness of the cast manganese bronze, its remarkable uniformity and excellence and the fact that there was so little difference between it and the hot rolled grades as to physical characteristics, discouraged the use of wrought manganese bronze in many quarters.

As a rule, however, designing engineers consider forgings more reliable than castings, and they ascertained also that wrought manganese bronze has much greater strength and ductility than yellow brass, Muntz metal, Tobin bronze, etc. Hence forged manganese bronze began to be used in various water supply and irrigation projects. Forgings over 3¾ ins. in diameter, more than 20 ft. long and weighing over 900 lbs. have been successfully made. There is no record that any of these forgings have proved unsatisfactory or have failed in service.

Other applications are for piston rods, shafting, axles, etc., for machinery to be used in mines where there is corrosive water, or on shipboard for turret parts in connection with gun mounts, ordnance attachments, etc., where the metal must resist corrosion by sea water.

A very soft, tough grade is used for sheet metal which has found application in the hulls of racing yachts, staybolts for locomotives and other bolts that must resist shock or the effect of repeated stresses.

Extruded manganese bronze blades have found some application in steam turbine construction where the erosive action of high pressure steam is very severe.

A large amount of wrought manganese bronze is used by powder and explosive manufacturers in situations where strength and non-corrosiveness is demanded, or where the use of steel would be dangerous by reason of its giving off sparks when struck.

Composition.—Wrought manganese differs chiefly from the casting grade in being free from aluminum. The addition of aluminum enables the alloy to be cast satisfactorily in sand molds. The following specifications as to composition may be considered as representative of the manganese bronze alloys most generally used:

Grade.	No. 1 A (for bars)	No. 1 B (for sheets)	No. 2 (for sand castings)
Aluminum	nil	nil	.15
Copper	57.35	58.15	56.00
Iron	1.40	.75	1.40
Lead	.03	.03	.03
Manganese	.02	.02	.12
Tin	1.20	.45	1.05
Zinc	40.00	40.60	41.25

Pure Metals Necessary.—In order to secure ductility as well as high tensile strength, extreme purity of the materials used is absolutely essential.

The grade of copper used in England is known as "Best Selected." It is of good quality, except that it contains antimony and arsenic which harden and lower the ductility of any alloy in which the copper is used.

In the United States, opinion as to which is the best grade of copper, is somewhat divided. Non-arsenical Lake copper is usually preferred for particular work because of its uniformity in quality, although the best grades of electrolytic copper are of equal analytical purity. The impurities usually present are as follows:

COPPER ANALYSIS.

	"Best Selected."	"Lake."
Antimony	.019	nil
Arsenic	.023	nil
Copper	99.895	99.881
Copper suboxide	trace	.112
Iron	.056	.004
Lead	nil	trace
Silver	.007	.003
Sulphur	nil	trace

In the manufacture of managaneze bronze the selection of a pure grade of zinc is perhaps more important than any other one consideration. Freedom from lead is essential as lead oxidizes readily and makes drossy brittle metal. Absolutely pure zinc would be an ideal material, and while it can be and has been produced commercially, its high cost has militated against its use. Dr. Jos. W. Richards made several tons of electrolytic zinc a few years ago in Philadelphia, but no market could be found for it.

A very pure zinc is produced in Eastern Pennsylvania from a willemite or silicate of zinc ore. The concentrate used contains garnet, rhodocrosite, red oxide of zinc and Franklinite. The ore will average

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*Paper presented at the annual meeting of the American Institute of Metals, Sept. 28 to Oct. 1, 1915, at Atlantic City, N. J.

49.26 per cent zinc and 3.50 per cent manganese. The slab zinc is marketed under various names, and it produces a manganese bronze of remarkable strength and ductility.

A zinc of almost equal purity is produced by the double distillation of galvanizer's dross, the slabs being skimmed just before setting so as to remove any impurities that rise to the surface. While there is little difference in the analysis of zinc made from willemite and that made from dross the former has the greater toughness and strength. Perhaps this is due to the manganese in the ore. At any rate, if samples of the two grades of zinc of almost identical analysis are cast into slush molds, the one casting is liable to crack and the other will not. For this reason, makers of intricate slush zinc castings are compelled to use the willemite zinc. A number of the makers of high grade zinc use the slush mold as a means of testing their product, and it will be found a very satisfactory way of testing zinc to be used for making manganese bronze.

The ordinary grades of spelter known as "Prime Western" are high in lead and for this reason should never be used. Scrap zinc reclaimed from sheet, etc., is also poor material. It may be high in lead and tin because of having been soldered, or it may contain much cadmium, which element has a hardening effect on manganese bronze. The grade of spelter used in England in conjunction with "Best Selected" copper is a French spelter known as Font-d'Art.

The following analyses indicates the composition of the grades of zinc discussed above.

SPELTER ANALYSES.

	Font-d'Art.	Electrolytic.	Willemite.	Dross.	P.W.	Scrap.
Aluminum	...	.0005	nil	nil	nil	...
Antimony	...	nil	nil	nil	trace	...
Arsenic	...	nil	nil	nil	trace	...
Cadmium	.123	nil	.002	nil	.024	.003
Copper	trace	.0120	.001	nil	.001	.060
Iron	.020	.0003	.003	.009	.024	.030
Lead	.135	.0193	.039	.057	1.448	2.050
Silica	...	.0009	nil	nil	trace	...
Tin	...	nil	nil	nil	nil	1.410
Zinc	99.718	99.9670	99.955	99.934	98.503	96.447

Melting.—Crucibles are generally used for making forging manganese bronze, the heats being 325 lbs. each and requiring a No. 125 crucible. More recently there has been a tendency to use a No. 300 crucible, as the smaller crucibles limit the output. Another reason for using the large crucibles is that when a number of furnaces are attached to the same stack there are variations in the draft and it is seldom that any two crucibles can be brought out at the same temperature.

The copper is first melted, then superheated, keeping it carefully covered with charcoal all the while. Next the iron and manganese additions are made from a small crucible in which they have been separately melted. Finally the zinc is added a little at a time with constant stirring and the alloy poured into ingots, for melting. The remelting is considered necessary to secure a more uniform distribution of the iron and manganese. If the initial temperature of the copper is not high enough, or if the zinc is added too rapidly, the iron addition is thrown out of solution to a greater or less extent and is found disseminated through the ingots in the form of small shot which are practically high carbon tool steel. These shot will knock the edge from a machining tool in a few minutes and cause cracks in a forging when it is stressed. The composition of these shot is indicated below:

Aluminum	nil
Carbon, combined	4.34
Carbon, graphitic	.66
Copper	3.82
Iron	89.44
Manganese	trace
Phosphorus	.010
Silicon	trace
Sulphur	.020
Tin	.110
Zinc	.870

It is not difficult to obtain a uniform alloy, however, if due regard is had to the temperature of the copper. The copper must not only be hot, but very hot, as it is much easier to make bad metal by underheating than by overheating.

Where the ingot metal is remelted for pouring into slabs or billets, reverberatory furnaces can be used if intelligently handled.

The only entirely satisfactory method of melting manganese bronze is in the open flame, oil fired type of furnace. The melting loss is low, the additions can be thoroughly alloyed and the metal poled and worked so that remelting is entirely unnecessary and the metal can be poured into billets at once without the usual double melting loss. Large heats up to 20,000 lbs. can be made and the resulting economy is considerable.

Pouring—The removal of dross from manganese bronze that is poured into slabs may be accomplished by skimming the slabs just before the metal solidifies.

In making large ingots, a crucible with a hole in the bottom, may be set on top the ingot mold and by keeping the crucible partly filled with molten metal, the entrance of dross is prevented. When the metal is poured, there should be as little drop as possible, for a long drop results in forming much dross. Hence, ingots should be short and thick if possible. Bottom pouring would be a good thing, only it would give cold metal at the top of the ingot and result in the formation of long pipes. With care a discard of only 2 per cent from the top of the ingots is possible. As the surface of the ingots is liable to be rough and full of cold-shuts, the ingots must be overhauled or rough turned before forging or rolling in order to avoid blister or slivers in the finished product.

The pouring temperature of the bronze must not be too high or it will cut the molds and become contaminated in this way with cast iron.

In time the ingot molds become coated with a layer of metallic zinc mixed with zinc oxide which has sublimed from the red hot ingots and condensed on the face of the molds. Unless this deposit is removed by scraping the molds or heating them to a red heat in an annealing furnace, the quality of the ingot metal soon deteriorates. The zinc seems to diffuse through the ingot in a remarkable manner, possibly being deposited along the margins of the crystal gains in the form of metallic zinc and makes the bronze less ductile. At times, too, this layer of zinc on the mold will produce such a volume of zinc vapor when the bronze is poured that the ingot is full of blow holes.

Forging—Manganese bronze can be readily forged, drop-forged, rolled or extruded as a red heat. The physical characteristics will depend on the finishing temperature. The material hardens rapidly when worked cold, and machinery designed for the cold rolling and drawing of Tobin bronze, Muntz metal and yellow brass is not usually powerful enough to handle manganese bronze properly. This may result in the exterior of an article being overstrained while the interior is soft and comparatively unwrought. Excessive cold work on manganese bronze makes it glass hard and it may even become full of hair cracks and incipient fissures invisible to the eye, but capable of being shown by stressing. An infallible test for excessive cold work on material otherwise of good quality is the appearance of the fracture of a test piece. If cup-shaped or lipped like the fracture of a salt steel specimen, assurance may be that the manganese bronze has been given the proper heat and forging treatment. If, however, the fracture is conchoidal and irregular, excessive cold work without proper annealing is indicated.

Other Grades of Forging Manganese Bronze—As the number of firms making manganese bronze has increased, there has been more or less competition for the business available and the quality of the metals used in the bronze has not always been as high as it should be. This has resulted in lessened ductility. Another cause for this fault is the desire for a higher tensile strength on the part of some designing engineers. To meet this demand, manufacturers have resorted to various plans which gave bronze of a higher tensile strength and elastic limit, but always with less ductility.

One manufacturer uses the casting grade of bronze, melts in an open flame furnace and poles the metal until a part of the zinc is removed and much of the dross and dirt. This gives an extremely clean and tough metal for sand castings, but it is not especially suitable for forging, as there is always some entangled alumina in the bronze that cannot be removed and which may cause defects. Further, this grade of bronze hardens too rapidly when hammered and hair-cracks are nearly always present in the finished forging unless unusual care is observed.

Another maker uses one-half casting mixture and one-half forging mixture with the addition of a little extra manganese. A tensile strength of over 90,000 lbs. is thus secured but the objections noted above hold good also for this mixture.

Other manufacturers have increased the aluminum by several per cent or the manganese or both, and have made additions of vanadium, titanium, etc., obtaining in this way a tensile strength as high as 125,000 lbs. per square inch, but with an elongation that is seldom more than 20 per cent.

Any radical departure from the formulas given in the first part of this paper or the use of any but the purest materials can only result in inferior manganese bronze. Safety is not found in extremely high tensile strength, but in great ductility and in avoiding excessive cold working. A tensile strength of say 70,000 lbs. should not be exceeded. Great ductility allows more leeway in forging, but cold work is always objectionable, as it may result in hidden ruptures or later on in the so-called "season cracking." No manganese bronze, however ductile, in fact no wrought non-ferrous alloy whatever, can be said to be able to safely withstand excessive cold work that strains it above the elastic limit.

The future should see a more extended use of wrought manganese bronze. Its physical characteristics warrant a wider field for it. If those who manufacture it make quality the first consideration, and if those who use it specify it intelligently, it will find a wide application.

MODEL PORCELAIN FACTORY IN KIANGSI.

The following translation from the Chinese newspaper Kuo Ming Hsin Pao has been made for the U. S. Consul-General at Hankow, China:

> The King Teh Cheng porcelain manufactory in Kiangsi was established in the time of the Ming dynasty. It was an imperial concern, which supplied all the fine porcelain used in the royal palaces, so every year huge sums of money were spent for its maintenance and its products attained to a state of perfection. Later, manufactories were organized by the people and, on account of the lack of funds, their products were far inferior in quality. It is said this was the only place that preserved the ancient ways of making porcelain, with beautiful ancient colors and exquisite designs, to the present time. It was largely destroyed during the late revolution, and the various samples and patterns which were kept there were all partitioned among themselves by the great men of the republican period. Recently Mr. Ko, the customs taotai of Kiukiang, obtained direct sanction from the President and a grant of $20,000 gold to restart the works. This will be the national model manufactory of porcelain, and the productions will be limited to two special departments—one for the manufacture of porcelain of the highest quality to be used solely for presentation to the rulers of other powers as gifts, and one for the manufacture of articles for the supply of the market. The work will begin in the month of August.

Ching Teh Cheng is situated on the Yangtze River, near the open port of Kiukiang. Since 1396 the imperial porcelain factory has been located there, and the finest of Chinese porcelain has been produced, though the output has been small. It seems that the continuation of such a plant would be a commendable undertaking, as this is an art in which China has always excelled.

SULPHATE AND SULPHITE LIQUOR UTILIZATION.*

By DR. E. L. RINMAN.

The closing address at the general meeting of the German Association of Cellulose and Paper Chemists, held in Berlin recently, was a paper by Dr. E. L. Rinman, entitled, Work in the Field of Sulphate and Sulphite Waste Liquor Utilization, which was published in the *Papier Zeitung* of April 4, 1915. Dr. Rinman prefaced his paper with a few remarks on the subject of his work, in the course of which he stated that since 1908 he had been occupied in researches in connection with the possibility of recovering alkali from the waste liquors of soda or sulphate cellulose manufacture and at the same time obtaining valuable substances from the organic constituents of the liquors. The results of these researches, published in part in *Svensk Kemisk Tidskrift,* in the year 1911, he described as two processes, both of which have been conducted on a large scale. He also referred to his success last year in working out a process for the utilization of sulphite liquor, which has been for several months under test, on an industrial scale, at the expense of the Aktiengesellschaft Cellulosa. The reading of the paper then proceeded, as follows:

UTILIZATION OF SULPHATE LIQUOR.

One of my processes for the utilization of sulphate liquor, which was the first perfected, is so intricate that it does not appear to be suited for mill operation. It comprises the following operative processes: Precipitation of the humus substances by carbonic acid, recovery of the soda by ammonia and carbonic acid, distillation of acetic and formic acids, as well as of ammonia salts, recovery of the ammonia by calcium hydroxide, dry distillation of the calcium salts of nonvolatile organic acids with calcium hydroxide. Thereby there is obtained, in addition to the complete recovery of the alkali of the liquor by replacing the alkali lost by common salt, for one ton of cellulose, the following products: Humus substance, with 6,800 calories per kilo, 600 kilos (1,320 lbs.); calcium acetate and formate, 180 kilos (396 lbs.); acetone spirit, 35 kilos (77 lbs.); light oils, 35 kilos (77 lbs.); heavy oils, 20 kilos (44 lbs.).

The other processes for the utilization of sulphate cellulose liquor is based on the fact established by me that the dry distillation of soda or sulphate cellulose liquor, with the addition of strong alkalies—such as sodium and calcium hydroxides—conducted under joint action of an adequate volume of steam, resulted in the production of large quantities of valuable distillation products, such as acetone, methyl alcohol, ethyl alcohol, and oils consisting of higher alcohols, ketones, aldehydes and carbohydrates. That the difference between dry distillation of sulphate cellulose liquor without alkali and with alkali is highly important is revealed by the fact that by the dry distillation with joint action of steam, from liquor that contains no free alkali, but three to five grammes of acetone spirit are obtained to a kilo of wood, whereas the same liquor, combined with the proper quantity of alkali, yields under the same circumstances, by dry distillation, fifty-five to sixty grammes of acetone spirit to one kilo of wood.

In determining what alkali should be employed in the above indicated dry distillation and the quantity that should be used, the following facts are of importance: The liquor contains, broadly stated, two kinds of organic substances; one contains methoxyl and has its origin, therefore, in the lignin constituents of the wood; the other, on the contrary, is free from methoxyl $[O(CH_3)]$ and has its origin in the carbohydrates—the saccharine, starch and cellulose of the wood. The substances containing methoxyl yield the largest quantity of acetone spirit, especially methyl alcohol, if they are distilled with soda lye and not with calcium hydroxide. The best results have been obtained by working with a sodium hydroxide proportion of 60 percent of the organic substance. The substances free from methoxyl, on the other hand, yield the largest quantity of acetone, principally acetone with smaller proportions of ethyl alcohol, when they are subjected to dry distillation with calcium hydroxide and not with sodium hydroxide. The best yield is obtained by adding one and a half times as much calcium hydroxide as would be required to render the solution caustic. Consequently a liquor rich in substances containing methoxyl should be dry distilled with a mixture of sodium and calcium hydroxides. The best yield of valuable by-products is obtained, for instance, from the liquor resulting from the production of easy bleaching woodpulp, by subjecting the liquor pitch to dry distillation with one molecule of sodium hydroxide and three-fourths molecule of calcium hydroxide to one molecule of sodium oxide found in the liquor.

This process for the utilization of sulphate liquor is comparatively simple, as will be evident from the following brief description of it.

As digester liquor in cellulose digestion, there is employed soda lye, with 3 percent of sulphate of soda (calculated according to active alkali), experience proving that this produces just as good cellulose as the customary sulphate lye containing 30 percent of sulphate of soda.

To the resultant liquor an equivalent quantity of soda, in the form of recovered soda, is added and it is causticized with lime, also recovered in the process. The carboniferous lime sludge is filtered and the filtrate concentrated to 35° to 40° Beaumé.

This thick liquor, mixed with three-fourths of a molecule of calcium hydroxide, calculated according to the quantity of soda in the original liquor, is then transferred to an evaporating apparatus, such as is used in sulphite cellulose mills for the production of

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*From Paper.

"cellpech" (cellulose pitch), and therein further concentrated until, while hot, it is viscidly fluid.

This mass is subjected to dry distillation, whereby, for one ton of cellulose, the following products are obtained: Approximately 300 cubic meters of noncondensable gases of high fuel value; 125 kilos of acetone spirit, light and heavy oils; a retort residue of sodium and calcium carbonate of about 400 kilos, containing carbon.

The combustible gases supply so much of the fuel required to effect the dry distillation that only about 100 kilos of coal are needed per ton of cellulose.

This process has thus far not matured sufficiently to be used in practice, the accomplishment of the dry distillation presenting great difficulties, while disagreeable odors could not be avoided if the liquor was sulphurous. Where the liquors contained too small a quantity of sulphate of soda, cellulose of least satisfactory quality was to be expected. However, in the meantime, I believe I have solved the problem, both in regard to dry distillation and in relation to the bad odors. The dry distillation can be accomplished in ordinary wood-carbonizing furnaces, in which the heating, for instance, is effected by heat elements and the mass to be distilled off, in strata or layers of a depth of about 3 cm., is transported on trucks into the retort. The manner in which the bad odor is obviated I will not state here, but this much may be said, the process completely disposes of this problem in an inexpensive manner.

If the process designed by me for the deodorization of waste gases of distillation is applied to the vapors of the digester the bad odors ordinarily proceeding from it will not be noticed. As in working according to this method only small quantities—about 3 percent—of sulphate of soda are used, there arise no disagreeable odors, not even from the remaining branches of manufacture, and no bad smells are diffused in the vicinity of the mill.

UTILIZATION OF SULPHITE LIQUOR.

I now approach the discussion of my new process for the utilization of sulphite cellulose liquors. This is associated with my process for the utilization of sulphate cellulose liquor. The association occurs in the fact, discovered by me, that the organic substances of sulphite liquor, by certain treatment, can be transformed into the same organic substances that are formed when wood is cooked with soda lye, for which reason the organic substances from sulphite liquor can be utilized by the same plan of treatment as I employed for soda or sulphate liquor.

The process is conducted as follows: The sulphite liquor is mixed with so much slaked or unslaked lime as will make to one liter of liquor 22 to 25 grammes CaO. Then the liquor is boiled, first at a low temperature, then at 180° Cent., altogether for five hours. After this boiling, the precipitate produced in the liquor, consisting of humus substance and calcium sulphite, is removed from the solution by filtration. The residue is treated with sulphur dioxide solution, by which the calcium sulphite is transformed into calcium bisulphite, whereas the humus substance remains. The calcium bisulphite solution is employed in making up fresh quantities of digester lye. The humus substance residue can best be freed from the water it contains by heating with hot water, it then forms a cake, containing 40 to 45 percent of water. The alkaline filtrate, obtained after separation of the humus substance and the calcium sulphite, and which contains the remaining organic substances of the sulphite liquor, chiefly in the form of oxy-acids, is evaporated to 40° Beaumé, and calcium oxide or hydroxide is then added in such quantity that to one molecule of CaO combined in the liquor there will be an addition of one and a half molecules of CaO.

This lime-impregnated liquor is evaporated to dryness and the dessicated mass subjected, in the presence of steam, to dry distillation. There is obtained thereby a distillate that contains acetone spirit, light and heavy oils and combustible gas. There also remains a dry distillation residue of calcium carbonate and carbon. In this manner, at the Skütskars Cellulosafabrik, from one liter of sulphite liquor which at ordinary temperature varied around 70° Baumé and which contained 0.9 percent total sulphur, the following products were obtained: Soluble calcium sulphite ($CaSO_3$), equivalent to 13.5 gm. SO_2 for sulphite digester liquor, 25 gm.; humus substance (anhydrous), 50 gm.: lime salts, 66 gm.

From the lime salts by dry distillation was obtained: Acetone spirit, containing 65 percent of acetone, 33 gm.; low boiling oils, 3.3 gm.; high boiling oils, 2 gm.; dry distillation residue, containing 6 gm. carbon, 46.2 gm.; variable quantities of combustible gases.

From five cubic meters of sulphite liquor there was consequently obtained: Calcium sulphite, 125 kilos (275 lbs.); humus substance, 250 kilos (550 lbs.); lime salts (limed), 330 kilos (726 lbs.), which yielded: acetone spirit, 16.5 kilos; low boiling oils, 15 kilos; high boiling oils, 10 kilos; lime carbon, 231 kilos, with 30 kilos of combustible carbonaceous gases.

In utilizing sulphite liquor, we can proceed by first fermenting it and distilling the resultant sulphite alcohol, then my process, as above described, may be employed with the mash obtained. The process in such case is conducted in the same manner as in utilizing the sulphite liquor without extracting the alcohol, excepting that from the mash a smaller quantity of lime salts is obtained for dry distillation. From mash at the Skutskärs Sulphite Alcohol Works there was obtained, for instance, from five cubic meters of sulphite, only 225 kilos of lime salts for dry distillation.

The process described can be conducted in a different manner, according to whether the sulphite mill has wood chips, sawdust, peat, etc., at its disposition. If thin chips or sawdust are available, these can be added, with great advantage, to the sulphite liquor, when boiling it with lime; the addition of lime must, however, in such case be suitably increased, because in cooking with lime at such a high temperature as is in this case employed we can obtain from sawdust on average 16 percent of its dry weight in the form of such lime salts as yield, on dry distillation with lime, acetone and alcohol. To one cubic meter of sawdust, having a dry weight of 145 kilos, we can therefore allow an addition of six to seven kilos of CaO. The addition of one cubic meter of sawdust to one cubic meter of sulphite liquor, on cooking it with lime, increases the lime salts, in round figures, by forty kilos. The addition of sawdust is moreover advantageous in other respects. The particles during lime boiling become so saturated with deposits of humus and calcium sulphite that filtration is greatly facilitated. The precipitate can then be filtered and washed in ordinary diffusers in the same manner as the cooked cellulose. When the precipitate, consisting of sawdust, monosulphite and humus, has been freed from calcium sulphite, it can be briquetted and coked and we then obtain a somewhat sulphurous coke which in fuel value is about comparable with wood charcoal.

In cooking sulphite liquor with lime and sawdust, we must, as indicated, so gauge the quantity of liquor that to one cubic meter a cubic meter of sawdust is allowed. If the sulphite mill has not such large quantities of sawdust at its disposal, the sulphite liquor, before the calcium hydroxide cooking, must be so concentrated that the cubic volume of sawdust equals the cubic volume of liquor. The sulphite liquor must not be concentrated to more than 35 percent of its cubic volume prior to the lime cooking, whether sawdust is available or not.

As I have already stated, where wood waste is available, the precipitate, consisting of wood substance, humus and calcium sulphite, can easily be filtered and washed in ordinary diffusers. The dissolving of the calcium sulphite out of this precipitate, with the aid of sulphuric acid, as well as the washing out of the resultant acid calcium sulphite, can be effected in the same diffusers, but they must of course be made acid-proof, lined with lead for instance. If on the other hand there is no sawdust available, the sulphite liquor is first concentrated to 35 percent of its volume and then subjected to lime cooking. The deposit of humus and calcium sulphite thereby obtained cannot very well be filtered in the diffusers, but is best washed and filtered in a centrifugal machine. If the centrifugal is acidproof the deposit, after the alkaline liquor has been expelled from it to a desired degree, may be treated directly—without stopping the centrifugal—with sulphuric-acid water for dissolving and washing out the calcium sulphite.

This process has recently been subjected in the Skutskärs works to a large number of tests on a wholesale scale. In these, partly mash from the sulphite alcohol works and partly sawdust have been used as raw material. Up to the present time, 500 cubic meters of mash with 500 cubic meters of sawdust have been treated. The lime cooking was undertaken in the rotary digesters of the sulphate cellulose mill, which have a capacity of thirty cubic meters. For each cooking, sixteen cubic meters of mash and sixteen cubic meters of sawdust were used, to which was added 400 kilos of unslaked lime. The cooking was conducted for the first half hour at a little over 100° Cent., then for one hour at 150° Cent. and finally for three hours at 180° Cent. After the cooking was finished, the pressure was let down and then the contents of the digesters were blown into the diffusers. From the gases blown off there were obtained for the cooking 10.5 kilos of wood alcohol and the usual quantity of oil of turpentine.

Washing in the diffusers proceeded smoothly and the liquor passing from them was perfectly clear. The washing was stopped as soon as the density of the liquor began to decrease. This is of importance because by this means loss of calcium sulphite by solution is prevented. The organic salts that are not washed out are returned for cooking after the calcium sulphite has been dissolved away; they combine with the sulphite liquor and are by this means recovered for subsequent dry distillation. As the diffusers were not lined with lead in the experiments conducted on a large scale, the material in them could not be washed with sulphuric-acid water, and this work was consequently performed in a smaller diffuser installed for the purpose. Washing with sulphuric-acid water proceeded most satisfactorily when the mass, before washing, was steeped for an hour in the acidified water. The liquor from the diffusers was concentrated in a vacuum apparatus to 25° Baumé, then treated in mixers of six cubic meters capacity, at about 90° Cent., with slaked lime. The liquor thus limed was evaporated to dryness in a drying cylinder of 1.8 meters diameter. This drying cylinder turned out in twenty-four hours 550 to 590 kilos of lime salts containing 6 percent of water.

The lime salts were then dry distilled in a furnace formed of two superimposed, helicoid, connected chambers, into which every minute 2.3 kilos of mass were loaded. The dry distillation yielded a well carbonized, small-grained, dry distillation residue of porous carbonaceous lime. The distillate still contained some mercaptan, an objectionable feature which could be avoided in the manner referred to in the sulphate process. By the distillation there was obtained acetone spirit containing 67 percent of acetone, 30 percent of methyl alcohol and 3 percent of ethyl alcohol. In addition, light and heavy oils were obtained. The lighter oil, as shown by test, can be successfully used as fuel for gasoline motors.

The humus-sawdust, washed with sulphurous acid, was partly freed from water under a pressure of 80 kilos to the square centimeter, whereby a pressed material, containing about 40 to 45 percent of water, was obtained. These pressed cakes of sawdust and humus, when coked, produced coke of limited solidity, but when they contained twice as much humus as sawdust, yielded a durable coke. The durability of the coke was increased by the addition of humus substances, irrespective of whether it had been cooked with the sawdust or was added, wholly or in part, at the briquetting.

In bringing the reading of his paper to a close, Dr. Rinman said:

"Having concluded my communication, I hope I have made known to you a process which, in the future, will make a profitable utilization of cellulose liquor possible. The entire available volume of liquor cannot of course be made use of according to this process, the demand for acetone being limited.

"Judging by the experiments undertaken on a large scale and calculations of the cost, it is to be expected, however, that mills practising this method of utilization will make a profit out of the process and solve the waste liquor problem."

THE HEMP AND TOW INDUSTRY IN NEW ZEALAND.

The hemp and tow industry of New Zealand enjoyed a prosperous season from April 1 to June 30, 1915, although the grades did not measure up well to the standard. This was owing to the moist weather and heavy rains. The following table gives the number of bales of the leading grades of hemp and tow baled during the quarter, as compared with the corresponding quarter of 1914:

	1914. Bales.	1915. Bales.
Hemp:		
Good, fair	6,331	8,034
High-point, fair	10,976	14,533
Low-point, fair	5,517	4,009
All other grades	2,114	1,614
Total	24,938	28,190
Tow:		
First-grade	909	1,750
Second-grade	3,915	3,954
Third-grade	2,876	1,910
Condemned	308	208
Total	8,007	7,822

The average bale of hemp weighs 400 pounds, and tow from 150 to 200 pounds.

The exports for the quarter ending June 30, 1915, amounted to $842,999, as compared with a total of $781,438 for the corresponding quarter of 1914. The increased value in exports was due to higher prices prevailing.

The price of hemp that was quoted at from $82.73 to $87.60 per ton at the beginning of the year has advanced to good fair, $114.35; high point, $109.49; low point, $100.98; with tow at $43.79 for first grade, $38.93 for second grade, and $34.06 for third grade.

COMMERCIAL NITROGEN FIXATION: A POLEMICAL NOTE.*

By S. PEACOCK.

Seventeen years ago Sir William Crookes in his presidential address on "The Wheat Problem" to the British Association directed attention to the importance of nitrogen fixation as a factor of economic agriculture, and characterized it as "one of the great discoveries awaiting the ingenuity of chemists." Then, as now, agriculture provided practically the sole commercial justification for the exercise of such ingenuity of chemists; and, for such use, combined atmospheric nitrogen must be prepared to compete with the least costly forms of nitrogen-containing by-products and waste materials. The fertilizer industry of the United States uses annually somewhat more than 100,000 tons of combined nitrogen, computed as ammonia, and the annual increase averages about 8 per cent. The combined nitrogen recovered in the United States from the distillation of coal for various purposes may be stated as approximately 70,000 tons per year, with an annual increase of about 15 per cent; and this increase must be assumed to be practicable for several years to come.

As encouragement to commercial nitrogen fixation, it may be stated that many organic nitrogenous substances heretofore used in fertilizers are finding other and more remunerative uses; and with each year a stronger demand is made on sources of supply which must favorably affect nitrogen fixation. A serious limiting factor is the cost. To illustrate: to grow one bushel of wheat requires nearly 4 lbs. of nitrogen, which at present prices on the farm somewhat exceeds 60 cts. in cost. It is evident that the cost is practically prohibitive.

Agricultural nitrogen hunger has been a practical fact for generations, not because ample nitrogen could not be obtained, but because it cost too much. Practically, farmers resort to a form of nitrogen fixation by growing leguminous crops in rotation and otherwise, but unfortunately legume nitrogen is scarcely less costly than the commercial product. Commercially, the problem is clear and explicit; either the price of farm products must be materially increased, or the cost of combined nitrogen must be lessened. The former may or may not indicate a confession of incompetency on the part of industrial chemists; it is the problem we have to consider.

As a commercial undertaking, nitrogen fixation must remain substantially dormant so long as the ammonia produced as a by-product of coal distillation remains of such relative amount that it is capable of controlling the rewards of capital invested in nitrogen fixation. It may be accepted as a fact that no nitrogen fixation method has as yet been publicly proposed which can produce combined nitrogen as cheaply as coke by-product ammonia. However, many very promising processes have been suggested, and it is to be hoped that some one or more will prove successful. The paramount objective must be a producing cost at the factory not in excess of 4 cts. per pound of ammonia; such process will lessen the cost of bread and greatly expand the consumption of fertilizer nitrogen.

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*Paper presented at the 27th General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22-24, 1915.

It is doubtful if any process simply affecting nitrogen fixation will attain the necessary efficiency; it is probably essential to work out a combination process which not only fixes nitrogen, but also accomplishes one or more additional useful reactions. An illustration of such process is the complementary formation of calcium carbonitride and phosphorus nitride, using a mixture of phosphate rock and carbon, with but one heat effect.

With the low cost ammonia, oxidation processes will follow, solving the problem of cheap nitric nitrogen and such compounds as ammonium nitrate. The weak point of American industries generally is the enormous proportion of costs permitted to selling and distribution. Therefore, the concentration of associated values in final end products is an important factor. Thus, ammonium nitrate or ammonium phosphate are more economical than ammonium sulphate, calcium phosphate or sodium nitrate, as the latter carry constituents useless or worse than useless for industrial purposes.

As the fertilizer industry must be regarded as the chief support of nitrogen fixation, the end products must be suitable for fertilizer needs. This implies a product constant in composition, soluble in water, not deliquescent, and one whose component parts do not readily assume undesirable forms, such as a gaseous or insoluble form. It is essential also that, when mixed with other fertilizer materials, such, for instance, as potassium salts, no reactions may occur tending to make the mixture hard and lumpy, or in any way lessen its dry granular state; otherwise the material cannot be used in distributing machines, and thereby becomes practically worthless.

It may be assumed as a governing principle that a commercially successful nitrogen fixation process must give as an end product potassium nitrate, or ammonium nitrate, or primary ammonium phosphate; and, that the factory cost must not materially exceed 5 cts. per pound of combined nitrogen figured as ammonia. It is true that the present price is several times that; but, having in mind the competitive power of by-product ammonia and the vast prospective increase in the production of same, capital is not justified in supporting a nitrogen project under other conditions.

The host of synthetic ammonia processes, of which that of Dr. Haber is the best known example, can never become commercially important, though they may have a moderate local application.

From the point of view of somewhat intimate acquaintance with all the nitrogen fixation processes publicly known at this time, there is nothing in the above conclusions which should in the least discourage American technologists.

DETERIORATION OF FIRECLAY GOODS IN OVENS AND RETORTS.*

At the 1914 meeting of the Institution of Gas Engineers a question that aroused considerable interest was that of the damage to retorts or firebricks, caused by the presence of "salt" in the coals carbonized. Subsequent discussion has tended to enlarge the interpretation of "salt" beyond sodium chloride, and has introduced the phenomenon of disintegration by carbon. The examples of this corrosion are in most cases stated in a fragmentary manner, making it difficult to locate the causes of apparently contradictory experiences and opposed explanations. It is the aim of this paper to get as much as possible of the facts, and see whether they can be reconciled, or at least furnish a starting point for further observation. The complexity of the subject makes it necessary to sub-divide, and it is proposed to do this in two ways. First, as to retorts, distinct from coke ovens; and secondly, as to the fusion of bricks as distinct from their disintegration. It will help to a clearer understanding of the problem if a statement of the published facts be made, before attempting an explanation.

In 1910 there appeared in "Stahl und Eisen" an account of investigations by F. Schreiber, of Waldenburg, Silesia, into "the destruction of coke oven bricks and their causes." Schreiber gives, among his illustrations, a photograph of a chamber that had been heated very irregularly, and another that had been heated uniformly. In the former the bricks were much distorted and disintegrated, whilst those of the latter were better preserved. The effects of common salt, and other soluble salts, are discussed in the paper, and an illustration of a brick in its original condition, and after the working of the sodium salt, is given. The effects of carbon deposits upon bricks is referred to, and a brick from a coke oven that had cracked, owing to the formation of free carbon, is specifically considered.

From the illustration thereof, it is seen that the deposit formed a black, wavy band, 20 mm. wide, within the middle third of the brick, one side of which band was 40 mm. from one edge, and the other side 15 mm. from the other edge of the brick—in all 75 mm. = 3 inches nearly. It is thus described: "The examination of a piece of coke oven brick from a Westphalian works revealed a peculiar carbon deposit. A black layer, 20 mm. thick, entirely symmetrical and clearly outlined, and running through the piece of brick with uniform thickness. The separate layers of the brick showed this composition.

It is described as "symmetrically limited carbon deposition in a chamber brick produced by diffused pyrogenically decomposed hydrocarbons." It is also stated that silica bricks may be destroyed in a similar manner.

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*From an article by Thos. Holgate, in "Gas World," London.

Upon the general question, one opinion was that the deterioration was caused by chemical action, to counteract which the addition of silica to the coal is recommended, whilst the mixing of different kinds of coking coal in the charge might have a beneficial effect.

In 1913, Professor Oskar Simmersbach, of Breslau, contributed to "Stahl und Eisen" two papers, and of which, "The Change in the Chemical Composition of Coke Oven Brickwork," we now give complete: "Towards the molecular deposition of carbon in coke oven bricks through pyrogenic decomposition of the hydrocarbon, and thence originating the loosening of the brick construction, especially with acid materials, F. Schreiber has drawn attention to the possibility that even volatile iron combinations, *e. g.*, iron carbonyl $Fe(CO)_3$, may exert the influence on the quality of the bricks. From this results a direct decrease of the iron content from the hot-wall layer to the chamber-side layer. F. Schreiber, according to private information, in various experiments, demonstrated a change of iron contents, but only in the last layer of the heat-chamber side.

"The reason for this might, apart from brick material, be due to working conditions. The pressure in the oven chamber at the beginning of coking is quite different from that toward the end of the distillation, for at the beginning, because of the strong gas development, there is over-pressure in the chamber. Especially with coal rich in gas there is at the commencement strong over-pressure, so that then also the iron-carbon combinations towards the heating wall side can exert their effect on the brick material, whereas with the finish of the coking, with regard to the more or less existing porosity in the side walls, the procedure can be taken in the opposite direction."

Simmersbach refers to a paper "The Sulphur Content of Coal and Coke" for collateral evidence as to the instrumentality of iron carbonyl. In tracing the origin of the sulphur he found that in the various cokes examined that element appeared to be mainly from an organic source. Allied to this sulphur content was the one of iron content, because such a large proportion of sulphur is due to iron pyrites. He noticed that the results he obtained for iron content of coke, and of the coal from which the coke was obtained, did not agree. And this difference he attributes to the formation and loss of iron in the form of volatile compounds such as the carbonyls. He adduces, in support of his view, experimental data of Mr. W. A. Bradbury, who, in 1878, recorded the disparity in the iron content of the ash and of the coal from whence it came. Herr Simmersbach then says: "That iron carbonyl or similar compounds are as a matter of fact, found in coke ovens no longer maintain that uniformity in the percentage of iron in them first—the bricks on the heated sides of the ovens showing a considerable increase in their percentage of iron. This increase can be explained only in the following way: Volatile iron compounds, varying in amount with the pressure of gas in the oven, pass through the pores of the chamotte from the side of the chamber to the side that gets heated; there these volatile iron compounds were decomposed (literally, burned up) and deposited their iron. When the quantity of air available is large, but not adequate for rapid decomposition (literally, burning away)—and this is the case when coal testing by incineration in the gas-muffle—then, for this reason, iron carbonyl can very readily be formed in fairly large quantities."

In October, 1913, in "The Times," Engineering Supplement, Herr Zinck, of Halberstadt, was quoted,

TABLE II.—SHOWING CHANGE IN COKE-OVEN BRICK.

Place of separation in centimeters.	Number of piece of brick.	Iron per cent.	Carbon per cent.	Sulphur per cent.
12.0				
	V	1.18	0.193	0.077
8.0				
	IV	1.24	0.026	0.025
7.0				
	III	1.27	0.036	0.004
4.5				
	II	1.47	0.041	0.004
0.5				
	I	2.51	0.075	0.053
0.0				

NOTE.—The chamber side of the brick is at the place marked 12 centimeters, whilst the heating-wall side is at the place marked 0.0.

TABLE I.—CHANGE IN A COKE OVEN BRICK.

Name of oxide and chemical formula.	Upper layer, 40 mm. of brick. Percentage composition.		Inner black layer in brick, 20 mm. thick. Percentage composition.		Lower layer of brick which has been slightly eaten into. 15 mm. thick. Percentage composition.	
	As taken from oven.	After removal of carbon.	As taken from oven.	After removal of carbon.	As taken from oven.	After removal of carbon.
Silica, SiO_2	83.77	83.99	80.00	85.24	83.35	83.53
Alumina, Al_2O_3	12.69	12.72	11.08	11.81	12.73	12.76
Ferric oxide, Fe_2O_3	1.16	1.16	0.67	0.71	1.15	1.15
Magnesia, CaO	0.24	0.24	0.23	0.15	0.23	0.23
Lime, MgO	0.42	0.42	0.29	0.31	0.32	0.32
Potash, K_2O	1.56	1.57	1.58	1.68	2.01	2.01
Carbon	0.26	.....	6.15	.....	0.21	.....
Total	100.10	100.10	100.00	100.00	100.00	100.00
Ratio of weight of SiO_2 to Al_2O_3	6.60	6.60	7.22	7.22	6.55	6.55

under the heading "Corrosion of Gas Retorts," as the authority for the following: All coals contain a certain amount of sodium chloride, and apparently when this is decomposed, the basic salt (sodium hydrate) combines with the surface of the retorts and bricks, thus forming an injurious coating on the interior. The coating, being sensitive to the variations of temperature, cracks and opens, so that further quantities of the harmful fumes can enter, and in time the retort becomes covered with a crumbling substance of low fusing point. In the affected portions the proportion of silica is reduced by as much as 6%, while the harmful alkali impurities are increased by over 3%, this greatly aggravating the tendency of the material to "run." Fortunately the majority of gas making coals in general use contain only small quantities of sodium chloride, and thus the effect is not practically marked. This, no doubt, is the reason why the action has escaped notice up to the present. Experiments carried out in a coke oven plant showed that the use of 0.143% of salt in the water for washing the coal ruins the retort in 3 years, whilst 0.036% renders a refractory substance of little value after 5 years.

English Experiences and Opinions.—In June, 1914, Mr. T. J. Bywater, stated this corrosion due to salt "to be a very important matter, because he had seen retorts fused on the inside which were quite good on the outside, where they were exposed to the gas." At the same time, Mr. W. Chaney said that "in all coals we are dealing with in carbonization there is a constantly varying quantity of salt, and no matter how highly refractory the material may be, it seems that we should aim to get a substance which will withstand the action of salt. I understand that in America something has been done in this direction, and that they have been able to find a material which is not only highly refractory, but sufficiently suitable to withstand the effects of the salt. It is a lime-bound brick, instead of the usual clay-bound; and 10 tons of coal are capable of being carbonized within 16 hours."

In October, 1914, an anonymous writer in the "Journal of Gas Lighting," whom, for brevity, we donate as "E. C." referring to the serious corrosion of fire bricks in coke ovens, said that it is confined to certain districts, and its causes are usually regarded as the alkaline constituents of the coal, principally as sodium and potassium chlorides. "It does seem, however, to have been fairly definitely established that the corrosion is much more marked when fire bricks containing a high percentage of alumina are employed. This seems as if the salt in the coal attacked the alumina, and hence caused disintegration of the brick. When bricks containing 90 to 95 per cent of silica are employed, the corrosion is much less marked, and the absence of alumina in such bricks seems to be a confirmation of the theory that it is the alumina which is attacked."

Later, in the same journal, Mr. W. Colquhoun challenges the main contention just set forth, saying, "It is not 'definitely established' that corrosion of coke oven bricks is more marked when the bricks contain a high percentage of alumina, but the exact contrary." Thus, in South Yorkshire, where the coal is high in sodium, we find high fixed ammonia in the liquor, and oven brickwork with a very short life, owing to fusion. The change that takes place in the brick is shown in the following analysis of a brick strongly attacked and vitrified on its face by the action of the salt. It is quite clear that alumina does not enter into the changes that occur, and that potassium and sodium disintegrate the bricks by the production of a fusible silicate. It has been shown in "Stahl und Eisen" (Mr. Colquhoun doubtless referring to F. Schreiber's paper mentioned above) that the resistance of bricks to corrosion increases directly with the contents of alumina.

TAFLE III.—ANOTHER EXAMPLE OF CHANGE IN BRICK.

	The solid unvitrified portion of brick.	The vitrified face of brick.	Difference.
Silica, SiO_2	82.20	74.90	—7.3
Ferricoxide and alumina	13.40	13.20	—0.2
Lime, CaO	1.60	2.00	+0.4
Magnesia, MgO	0.40	0.70	+0.3
Potash, K_2O	0.40	4.35	+3.95
Soda, Na_2O	0.25	2.65	+2.40
Loss by ignition	0.10	1.00	+0.90
Total accounted for	98.35	98.80	....
Ratio SiO_2 to Fe_2O_3 and Al_2O_3	6.134	5.674	—0.46

No explanation has been found for the following fact: At colliery A, with 9.35 per cent of NaCl in the coal, there is no attack of the bricks; at colliery B, in the same county, there is found only 0.132 per cent; and the ovens have to be relined every two years. "In the United States, it must be remembered that the coking coals are dry (not washed) and low in alkalies. While lime-bound silica is the standard material there for coke oven construction, it has yet to be shown that it is suitable for the coking of washed coal, and suitable, also, for use with 'salty' coal."

The writer, "E. C.," replied to Mr. Colquhoun, reiterating his opinion, and saying. "But I make a distinction between vitrification and corrosion; and I have it on the authority of a responsible party, that bricks containing 92 per cent of silica have suffered no corrosion, while bricks containing 80 per cent have crumbled away."

Mr. Chaney also replied to Mr. Colquhoun's letter, stating his experience that the corrosion is less when a highly silicious brick is employed. This was most noticeable in an oven partly constructed of highly silicious bricks from the Continent, and English bricks containing about 14 per cent of alumina. The two types of bricks were chequered in the oven, and the corrosion in the material containing alumina was most marked, while the silica was intact. It may be that the refractoriness of the material plays an important part in the action of the salt, when combined with the wet coal at time of contact; but it demonstrates that the lime-bound siliceous brick is more suitable to withstand the combined circumstances applicable to coke oven practice.

In January, 1915, Mr. Colquhoun refers "to a phenomenon known, but not frequent, in coke oven practice, namely, the deposition of carbon in the pores of the brick, leading to its ultimate destruction. This occurrence is not unknown in gas-works practice, and certainly does not bear on the subject 'E. C.' originally introduced, when he stated that corrosion is more marked in bricks containing a high percentage of alumina. On the contrary, the resistance to salt increases directly with the alumina contents, and as the other bricks high in alumina are in extensive use in eastern Germany, coking salty coals; and they perfectly resist the action of salt. Aluminous bricks have qualities other than the resistance to salt, which render them less suitable than quartzite bricks for coke oven work. One of the most resistant bricks in a highly 'salty' neighborhood is the siliceous brick, of which an analysis is given above. There are factors as important as analysis, of course, but of these we have only a vague knowledge."

Having set forth the problem we proceed to investigate various data and to consider the various chemical and physical factors, to see how far they confirm the experiences described.

THE RESISTANCE TO CHANGE OF SILICA AND ALUMINA CONTENT.

At the International Congress of Mining Engineers, in 1910, Dr. Eugen Blasberg read a paper on "Changes in the Composition of Fire Bricks." There are ninety analyses of bricks tabulated in the paper, under three classes: (1) bricks from blast furnaces, cupolas, etc.; (2) coke oven bricks; silica bricks. Many of these are in sets, that is, they are analyses of parts of the same brick, some of which are believed to be unchanged and others obviously changed. The writer has taken all these analyses, and others, and computed the ratio by weight of the $SiO_2 \div Al_2O_3$ (silica to alumina

TABLE IV.—SHOWING CHANGES IN FIRE BRICK, WHERE ALUMINA HAS DISAPPEARED MORE LARGELY THAN SILICA.

	Cupola brick.			Brick from a briquetting furnace.		Coke over bricks				Silica bricks (Chequer bricks). From gas flue.		From air flue.	
	Core.	Intermediate.	Slag.	Core.	Slag.	Core.	Warty fused crust.	Core.	Corroded portion.	Core.	Slag.	Core.	Slag.
SiO_2	64.13	63.95	52.10	70.93	67.07	83.72	82.85	82.87	77.31	90.14	73.94	92.01	86.91
Al_2O_3	29.61	29.67	19.81	24.68	21.52	12.43	11.55	13.52	11.04	4.06	2.73	2.94	2.45
Fe_2O_3	1.89	1.93	1.39	1.48	5.02	0.98	1.00	1.15	3.71	1.98	10.81	1.94	6.25
CaO	0.80	1.10	0.52	0.15	0.90	0.15	0.27	0.26	2.00	2.66	4.24	1.90	1.10
MgO	0.72	0.75	0.47	0.19	0.54	0.24	0.32	0.31	0.81	0.17	0.91	0.21	0.19
K_2O	2.85	2.50	3.90	2.23	4.65	2.48	4.01	1.44	4.38	0.99	6.37	1.00	3.10
CuO	....	0.10	21.66	....	....	....	....	....	....	....	....	....	....
Lost in calcination	....	....	0.15	0.34	0.30	....	....	0.45	0.80	....	....	....	....
$SiO_2 \div Al_2O_3$	2.166	2.155	2.63	2.875	3.12	6.735	7.173	6.129	7.003	22.20	27.08	31.29	35.47

TABLE V.—COMPILED FROM THE DATA OF DR. BLASBERG, RELATIVE TO A SILICA BRICK, SHOWING ACCRETIONS AND DEPLETION.

Components (Sodium included as an equivalent of potassium).	Intact core.	Strongly corroded.	Black portion, white grains showing.	Grey portion, grains vanished.	Crystalline outside layer.	Exclusive of the manganic oxide.	Exclusive of ferric oxide and manganic oxide.		Exclusive of lime, ferric oxide and manganic oxide.		Exclusive of alkalies, magnesia, lime, ferric oxide and manganic oxide.	
	a	*b*	*c*	*d*	*e*	*e*	*a*	*e*	*a*	*e*	*a*	*e*
SiO_2	95.94	89.38	90.13	89.60	69.87	75.210	97.016	88.950	98.31	95.050	98.47	97.20
Al_2O_3	1.50	3.47	2.52	1.33	2.01	2.163	1.517	2.558	1.53	2.705	11.53	2.80
Fe_2O_3	1.11	2.73	3.80	5.15	14.35	15.446	......	......	......	......	.....	.....
CaO	1.30	3.80	2.52	2.18	4.26	4.586	1.315	5.423	......	......	.....	.....
MgO	0.11	0.24	0.75	1.00	1.14	1.228	0.112	1.452	0.115	1.535	.....	.....
K_2O	0.04	0.38	0.24	0.62	1.27	1.367	0.040	1.617	0.045	1.710	.....	.....
Mn_3O_4	....	.....	.....	.....	7.10	......	......	......	......	......	.....	.....
Loss in calcinations	....	.....	0.04	0.12	.....	......	......	......	......	......	.....	.....
$SiO_2 \div Al_2O_3$	63.96	25.76	35.77	67.37	34.76	34.76	63.96	34.76	63.96	54.76	63.96	34.76
Column number	1	2	3	4	5	6	7	8	9	10	11	12

TABLE VI.—SHOWING THE ACCRETION OF ALKALIES AND DEPLETION OF ALUMINA, ETC., IN CUPOLA BRICK, PER TABLE IV.

Components. (Sodium included as an equivalent of potassium.)	Exclusive of copper oxide. Core.	Slag.	Exclusive of copper oxide and alkalies.		Change per cent of original percentages.	Exclusive of copper oxide, alkalies, lime and magnesia.		Exclusive of copper oxide, alkalies, lime, magnesia and ferric oxide.	
	a	*c*	*a*	*c*		*a*	*c*	*a*	*c*
SiO_2	64.13	66.63	66.01	70.13	+ 6¼	67.06	71.07	68.42	72.45
Al_2O_3	29.61	25.34	30.47	26.67	—12½	30.95	27.03	31.53	27.55
Fe_2O_3	1.89	1.775	1.95	1.87	— 4	1.99	1.90	.....	.....
CaO	0.80	0.665	0.82	0.70	—15	.....	.....	.....	.....
MgO	0.72	0.60	0.74	0.63	—15	.....	.....	.....	.....
K_2O	2.85	4.99	......	.....	......	.....	.....	.....	.....
$SiO_2 \div Al_2O_3$	2.166	2.63	2.166	2.63	......	.....	.....	.....	.....
Column number	1	2	3	4	5	6	7	8	9

ratio). This has been done to find out if there was any loss of alumina to be traced in the different specimens. A number of cases show an unmistakable loss of alumina. It is known to those who have studied the interpretation of such analyses that, owing to the obvious accession of certain ingredients and the obvious depletion of others, it is not easy to see whether the remaining ingredients have been affected merely by this redistribution, or whether they also have been depleted or their content increased. The importance of this consideration is great, relative to the silica and alumina content, but it can be met by the device of comparing the silica-alumina ratio before and after a supposed change. This ratio will, of course, only tell us whether the silica or alumina have disappeared most, but this information will be very useful, and appears to be unequivocal. Out of 32 comparisons, 22 examples show the silica content to have disappeared most; 7, the alumina to have disappeared most, and 3 where the removal of silica and alumina has been about the same. In none of the investigations that the writer has studied, is there any allusion to an actual loss of alumina, or to a relative loss thereof; but the evidence of Table IV appears to be conclusive on this point, and leads to the question as to how the loss is effected. It is true that Mr. Chaney refers to the alumina being "attacked," but this does not appear to be synonymous with loss, as will presently be seen. The analyses furnished by Mr. Colquhoun show, by the ratio computed by the author, that, in this specimen, a loss of silica has occurred, that is if the combination of the ferric oxide with the alumina in his figures does not lead us astray.

Table IV gives the source and composition of six bricks that show a greater loss of alumina than of silica, manifest by the rise in the ratio, *i. e.*, the $SiO_2 \div Al_2O_3$; and Table V gives particulars of a silica brick that shows both classes of change in the analyses of its five sections; while Table VI shows the lessons to be obtained by comparing the first and third columns of Table IV.

Table V shows how, by a successive elimination from the computation of each oxide of an element, the various changes can be elucidated, concluding in the last two columns with the percentages of the silica and alumina in the two specimens of the silica brick, *a* and *e*. This comparison shows that *e* has lost silica and, consequently, appears to have gained in alumina, markedly brought into prominence by the change of ratio from 63.96 to 34.76. If a similar comparison be made between *a* and *d*, we shall perceive a change in the reverse direction. The first fact to note in reference to analysis *e*, column 5, is an absorption of manganic oxide (Mn_3O_4), and when this is removed from the computation, so as to eliminate a manifest accretion, we obtain column 6, which, in turn, shows, by accentuation, other accretions in ferric oxide, the alkaline earths and the alkalies. Removing the first named, we obtain columns 7 and 8, which show very large accretions of the alkalies and alkaline earths. Removing lime, we obtain columns 9 and 10, which show the accretions of magnesia, potash and soda in their true relations. [Although these accretions of the alkalies are large, they are surpassed by some found in the coke oven bricks of an English gasworks.] Finally, in columns 11 and 12 we have the silica and alumina content, showing that a relatively small loss of silica makes an apparent rise in alumina, defined by the ratio changing from 63.96 to 34.76. Of the five portions of this silica brick, the only one showing manganese is *e*, the crystalline outside layer, and this accretion has probably intensified chemical action, accelerating the other accretions, notably ferric oxide, the alkaline earths (lime and magnesia), and potash with soda.

Applying this mode of inquiry to the other portions, we find that specimen *d* shows no diminution of silica, but a slight loss of alumina, though the figures of 98.47 SiO_2 and 1.53 Al_2O_3 for the intact specimen *a*, and 98.54 SiO_2 and 1.46 Al_2O_3 for *d*, shows that in reality the silica and alumina contents have changed little, if at all. This fact is not obvious on inspection of the analytical data, and is perhaps too sharply accentuated by a change of ratio, but the ultimate percentages place the matter in its true light. The several portions thus examined give the ultimate percentages set out below, showing silica loss from *b*, *c* and *e*, and neither silica nor alumina appreciably removed from *d*. Of *b*, it must be remarked that with less accretions than in the case of *e*, there is greater loss of silica, agreeing with the description of its being strongly corroded.

Silica brick as in Table V.	Ultimate percentages of the five portions of brick.				
	a	b	c	d	e
Silica	98.47	96.26	97.39	98.74	97.2
Alumina	1.53	3.74	2.61	1.46	2.8

Having shown the utility of the method, we must now apply it to a case of the class where alumina has been lost in notable degrees, *e. g.*, the cupola brick of Table IV. The three portions thereof are: *a*, the apparently unchanged; *b*, just beginning to change; and *c*, the highly changed, with a marked accession of copper oxide.

Only *a* and *c* need be dissected, and doing so will show the changed aspect of the analysis when the copper oxide is eliminated, and the incidence of the potash and soda accretion. These are shown in columns 1 and 2 of Table VI, then in 3 and 4, while in column 5 it is shown that, relatively, rather more lime than magnesia, viz., 15%, each has been lost than alumina—12.5%. Continuing, we find in columns 6 and 7, that the loss of ferric oxide has been, relatively, smaller than the loss of alumina, whilst in columns 8 and 9, we see that a loss of 12.79% of the original alumina—from 31.58 to 27.55—has brought about the apparent rise of 5.89% of the original silica from 68.42 to 72.45. The clue to this loss of alumina is in the change of ratio from 2.166 for specimen *a*, to 2.63 for specimen *c*, and its magnitude expressed as percentages is seen in columns 8 and 9 of Table VI. Proceeding to the remaining specimens of Table VI, and computing in the manner just shown, we obtain the results in Table VII, which shows the amount of alumina in each 100 parts of silica-alumina before and after the use of the brick; and in the last column the percentage of loss of the alumina over that of silica (if any) based upon its original content.

TABLE VII.—SHOWING THE CHANGE IN THE COMPOSITION OF BRICKS, WHEN THE IMPURITIES AND ACCESSORIES ARE ELIMINATED FROM THE ANALYSIS.

Nature and source of brick, per Table IV.	Percentage of alumina in the silica-alumina part of the brick.			Alumina lost in percentages of original (intact) content.
	Intact.	Changed.	Difference.	
Cupola brick	31.58	27.55	4.030	12.79
Briquetting furnace brick	25.807	24.272	1.535	5.95
Coke oven brick	12.928	12.235	0.693	5.45
Coke oven brick	14.027	12.495	1.532	10.92
Silica chequer bricks				
From gas flue	3.855	3.561	0.324	8.34
From air flue	3.097	2.750	0.347	11.21

The loss of alumina in each of these six specimens is pronounced, and appears relatively almost as great with the one containing the least alumina originally as with the one containing the most. The diversity of working conditions is as large as that of the chemical composition, and the evidence appears to be conclusive, however unexpected, that under certain circumstances alumina is lost from fire bricks.

THE CHANGES IN BRICKS OF THE BIRMINGTON COKE OVENS.

We now look to see how the foregoing facts stand in relation to Mr. Chaney's experience. A brick before use contained 75% of SiO_2 and 21.6 of Al_2O_3, which in time was reduced to 55.8 of silica and increased to 41.37 of alumina. The important fact is here revealed that the brick relatively rich in alumina, which Mr. Chaney finds has suffered more than the one relatively rich in alumina, has perished not by loss of alumina, but by loss of silica. Dealing with these figures, similarly to Table VI, we find that, excluding all other constituents, the comparison stands as follows:

	Before use.	After use.
Silica	77.64	57.43
Alumina	22.36	42.57
	——	——
Ratio	3.472	1.349

The contrast is so great that it at once raises the question as to how the presence of alumina can contribute to a chemical action that results in the loss of silica. If the analysis were more complete, we might be able to trace some clue, but in the absence of such information, we must direct attention to another brick, of which Mr. Chaney gives the following particulars. Analysis of the surface of fire brick: The original material contained 70% of silica and 0.7% of sodium or potassium chlorides. At the end of two years the potassium and sodium chlorides had increased to 8.4%, and the structure of the brick on the surface was destroyed. The accession of alkalies agrees broadly with the large amount given by Mr. Colquhoun, when one remembers that Mr. Chaney's figures are expressed as chlorides, whilst Mr. Colquhoun's are as oxides. It will be noted that this brick contains less silica than the one previously mentioned by 5%, and presumably more alumina, but in the absence of a complete analysis the ratio of SiO_2 to Al_2O_3 cannot be discussed. The remarkable accession of the chlorides, and the well-known chemical activity of aluminum chloride, lead one to inquire whether the last-named substance may be an intermediary in the mischief.

There are reasons, based upon the facts set forth in our introduction, why we should not exclude from consideration the oxide of carbon, the hydrocarbons and water present in the coke oven or the heating flue (which questions are discussed later); and towards these gases aluminum chloride is a powerful catalyst.

THE ROLE OF ALUMINUM CHLORIDE, CARBIDE, ETC.

The last edition of the Encyclopedia Britannica states, "As a synthetical agent in organic chemistry, aluminum chloride has rendered possible more reactions than any other substance; here we can only mention the classic synthesis of benzene homologues." To the modern chemist the acceleration of chemical action, by the presence of aluminum chloride, is known as the "Friedel and Crafts' reaction," and during recent years much attention has been paid to determine the conditions under which the greatest speed of reaction takes place. There are many points as yet unsettled, but two are apparently established, viz., (*a*) that the accelerating effect of aluminum chloride is roughly in proportion to the quantity present; (*b*) that if the aluminum chloride enter into certain combinations, its effect upon surrounding substances is diminished. The importance of the first of these points, in relation to the present discussion, is obvious, for although many of the chemical reactions induced by aluminum chloride leave the quantity of that substance free and unchanged, yet the quantity present does effect the rate at which the reaction will proceed. This is a factor that must be borne in mind, because the conditions inside the retort or coke oven are constantly varying, and time is of the essence for carrying out of a particular reaction. Of the second point, it must be noted that circumstances in certain retorts may be such as to favor combination, whilst in others not, bringing about a contradiction in results where, apparently, the same conditions prevail. One particularly well-known combination of alumina chloride, viz., that with common salt, forming the double chloride of ammonium and sodium (Al_2Cl_6, $2NaCl$), is most likely to occur. If it does, we have a substance which melts at 185° C., and volatilizes at a red heat. Moreover, it may reasonably be inferred that it would react with silica, producing the readily fusible silicate of sodium, accounting for the loss of silica. The behavior of aluminum chloride depends, in some cases, upon its being anhydrous—that is, after a charge of wet coal, its effect might differ from what it would be later, when all moisture had been expelled by heat.

Schrieber and Simmersbach have referred to the effect of metallic carbonyls as did, at a prior date, Mr. Frank Firmstone, but, so far, a carbonyl of aluminum has not yet been found, whilst on the other hand the carbide (Al_4C_3) does exist. It has properties of importance in this connection, for it is formed by the action of carbon, or the oxides of carbon, on alumina at very high temperatures, and is remarkable as being staple at high temperatures, and yet undergoing decomposition at a dull red head. In contact with water or dilute acids, it reacts slowly with the production of methane. Up to 1,400° C. the carbide acts as a reducing agent on metallic oxides, and this may operate on the oxides of iron present in fire bricks.

The behavior of alumina towards carbon and carbon monoxide is largely conditioned by the temperature, and at the higher temperatures aluminum reacts with metals, producing an alloy. The oppositeness of this reaction is seen in the case (see Table IV and detail in Table VI) where alumina was removed from the brick where copper had gained access to the walls of the furnace.

It is desirable here to note that when carbon bisulphide vapor is passing over strongly heated alumina, aluminum sulphide (Al_2S_3) results. It forms a yellow fusible mass, which is decomposed by water into alumina and sulphuretted hydrogen.

THE ROLE OF IRON CARBONYL.

In his explanation of the variation of iron content in the 5 parts of a brick, Simmersbach refers to volatile metallic carbonyls, meaning, doubtless, those of iron, and specifying one as $Fe(CO)_3$. This formula is probably a slip of the pen, for the three known are the tetracarbonyl, $Fe(CO)_4$, the penta, $Fe(CO)_5$, and the differo-nona, $Fe_2(CO)_9$. The penta carbonyl is the one best known, and is the one proved to be present in coal gas, and, to a greater extent, in water gas. It is produced, at a low temperature, by the action of carbon monoxide on finely divided iron, yielding a liquid that boils at 103° C. One property that must be noted here is that it is diamagnetic.

Neither Schrieber nor Simmersbach, in the papers quoted, give experimental proof that the loss of iron and the accession of carbon are due to the agency of iron carbonyl, but the conjecture appears not unreasonable, for Fe(CO) could be produced at a low temperature and decomposed at a high one, with separation of iron and carbon monoxide. From the latter could come finely divided carbon—from combustion in an atmosphere deficient in oxygen, and also by reaction with iron in its various forms of oxidation, and at suitable temperatures, usually of a moderate order. The figures given by Simmersbach (Table II) show with depletion in iron a notable accession of carbon, and a smaller one of sulphur on the chamber side, as against the heating wall side, but this degree of change is not the same as shown by the three intervening layers. What appears to be the important factor in the case, is the moving about of the iron and the carbon in the brick, whether iron carbonyl is the intermediary or not. The reduction in the state of oxidation of the iron of itself spells increased fusibility, while the carbon deposits mean disruption, allowing hostile influences to gain easy entrance to the brick. Further, the finely divided carbon is itself a powerful reducing agent upon oxides of iron, and would accentuate the mischief.

THE EFFECT OF IRON AS A FLUX, IN RELATION TO SILICA AND ALUMINA CONTENT.

The injurious effect of iron just discussed must be considered as affected by different ratios of alumina and silica. It is known to clay workers that a given amount of ferric oxide would promote fusibility in a different degree, according to the presence of other fluxes, and also to the ratios of the concomitant alumina and silica. This last named phenomenon has been quantitatively examined by Mr. C. S. Kinnison. Ferric oxide cannot exist above 1,350° C., but dissociates into oxygen and magnetic oxide, which latter, in presence of silica, as in clay, forms ferrous silicates, dark brown to black in color. This color change was taken as criterion of the reduction of ferric oxide when added to various clays. The results show the temperature of formation of ferrous silicate is qualified by the $SiO_2 \div Al_2O_3$ ratio of the body mixture, the greater the quotient of the $SiO_2 \div Al_2O_3$, the lower the temperature. The tests were carried out on mixtures where the ratio, as just defined, varied from 2 up to 9. Thus, in acid clays, reduction of Fe_2O_3 takes place at lower temperatures than in more aluminous bodies—1,320° as compared with 1,390° C.; and when fluxes are present the dissociation temperature is 1,210° to 1,220° C. The application of this recently acquired data to our problem would be that if a silica brick, either by its original or acquired iron content, contained as much thereof as a more aluminous brick, fusibility would be increased to a greater extent.

THE TENDENCY OF SILICA TO CHANGE ITS VOLUME.

The quality of a silica brick is not wholly—although largely—defined by its chemical analysis or melting point, for, according to K. Endell, the best samples of raw material contain a silicious cement, which can be detected by the microscope, and which binds the quartz grains together. "Owing to the fine state of division of any impurities, such quartz possesses considerable mechanical strength, and increases markedly in volume upon the first ignition. The silica content should average 96 to 98%." It is desirable to examine this statement, so that we may perceive their true bearing—and that of other quotations—upon our problem. And, first, we must try to avoid confusion in the use of a term employed in our introduction by Mr. W. Colquhoun, viz., vitrification. He presumably used it to denote that the surface of the bricks had been fused, and the material had "run." In ordinary commercial language, to say that a building brick had a vitrified surface is to imply, not a defect, but a good quality; whilst in scientific descriptions it is employed to denote the change of form from the crystalline to the amorphous—that is, from a granular to a glassy texture. It denotes a changed appearance, whether that be brought about by heat or by some other agency. The term is used in this last sense in the quotation we now give from R. Rieke and K. Endell: "All kinds of quartz glass devitrify and become crystalline on long heating at a high temperature. The resulting product is cristobalite, and the degree of devitrification may be ascertained by density determinations, the specific gravity of silica being 2.21 and of cristobalite 2.33. The extent of the change is dependent on temperature, time and surface. Under 1,200° C. it requires many hours to become apparent; towards 1,685° C. the melting point of cristobalite, it is nearly proportional to the length of heating. The least tendency to crystallization is shown by quartz glasses, which are quite clear and transparent and free from bubbles. Surface impurities held in suspension conduce to devitrification. The phenomenon is prejudicial, as it causes brittleness and permeability to gases, the transformation from silica to cristobalite being accompanied by a contraction of 5% in volume. At 230° C., in cooling, β cristobalite, the regular crystalline form, changes into the a variety, which accentuates devitrification."

K. Endell has given a series of photomicrographs of various silicas, showing which are most suitable for brickmaking, and these show the cement, the quartz, tridymite and cristobalite (three different crystalline forms of silica), and the effects thereupon of heating to 1,450° C. One of these shows a specimen of first-class material heated five times to 1,450° C., disclosing innumerable minute cracks, or fissures, passing through the cristobalite ground mass.

This valuable information is obviously most applicable to the manufacture and use of high percentage silica bricks, and in considering in what degree it can be predicted of others, it must be remembered that experience has shown that some of the properties can be modified by an intelligent blending of alumina therewith. All the evidence that we have marshalled leads to the conclusion that, whilst silica can be lost from coke oven bricks by fusion, yet it may be accompanied by disintegration brought about by depositions within the pores of the material. If, then, these hostile forces can be kept outside the brick by means of a close, homogeneous surface, much would be gained. It is not only the chemical nature of silica, but also the physical, that constitutes a fundamental difficulty, and we do not know that the admixture of alumina may not, at certain concentrations, introduce disturbing factors.

CARBON DEPOSITS DUE TO IMPERFECTIONS IN THE HEATING ARRANGEMENTS.

Some of the cases of coke oven trouble have been attributed to unequal heating, and this, whilst introducing mechanical stress by unequal expansion, may simultaneously bring about incomplete combustion in certain parts of the heating flues, tending to cause carbon deposits. These troublesome things may arise where the coke oven gas is employed for heating, or even when producer gas is employed, although the chain of chemical actions may differ. Yet again, they may be caused if the heating gas is passed (as is done in some types of oven) through recuperative flues *en route* to the heating flue.

ELECTRICAL CONSIDERATIONS.

Closely allied to the chemical and physical factors already mentioned is that of the discharge of solid particles carrying electric charges from hot bodies, notably carbon, the alkalies and alkaline earths and the metals. According to temperature these charges may vary in character from positive to negative. The most familiar example is that of the incandescent electric lamp having a carbon or metal filament, where the glass becomes blackened by the deposition of such particles. It is the blackening that limits the temperature at which the vacuum glow lamp can be worked, and an attempt to minimize this influence by filling the bulb with nitrogen constitutes the distinctive feature of the half-watt lamp. Sir Wm. Crookes has shown that by the electric furnace even the platinum metals can be vaporized, and the general phenomenon has been investigated by Prof. O. W. Richardson in its electrical aspect. That gentleman framed an equation in conformity with the theory of electrons, and his experiments and equation have been discussed by the aid of other experiments. The conclusion reached is that this "electrical sputtering" is largely increased when gases are present that may interact with the heated body. Amongst these gases are the oxides of carbon, and the occluded gases in carbon. Under these favorable conditions quite large currents of electricity are set up, and as retort and coke oven conditions are very similar to these, it is a reasonable inference that electric influences must be reckoned with. Dr. Kaye has given photographs showing how the particles of metal may be removed by the electric current, leaving a distinctly pitted surface, even when gases are excluded from contact therewith. It would appear, therefore, that whilst chemical action occupies the first place in the disintegration and removal of silica and alumina, yet this may be supplemented at high temperatures by something akin to evaporation accompanied by electrical charges. The gases of the coke oven or retort—internal or external—will in turn be affected by these electrical charges, doubtless becoming ionized and having their chemical activity stimulated. If iron carbonyl is present, as possibly it may under certain conditions, being diamagnetic, it would be expected to behave differently to the remaining gases, almost wholly of the paramagnetic class.

IMPORTANCE OF THE WATER USED IN COAL WASHING.

This ionization of the gases may also be affected by the constituents of the water being distilled, and be accompanied by sympathetic action on the brickwork. Sir J. J. Thomson has found a radioactive gas—probably a mixture of two hydrocarbons—to be frequently present in well-water, but not in any of the numerous samples of rain and surface water that he tested. One component of this mixed gas had a density of about twice, and the other between six or seven times that of CO_2, and when cooled became liquid, having a very strong smell of coal gas. The gas can diffuse through a porous plate, and that it is a hydrocarbon was shown by spectroscopic examination by Mr. Newall. The gas extracted from the water retains its radioactive properties after bubbling through strong sulphuric acid or caustic potash, after passing over red-hot copper, or through a narrow platinum tube kept at a white heat, and it does not seem appreciably affected when sparks are passed through it.

Seeing that most of the coal converted into coke in this country is first washed, and that at many collieries pit water is used for the purpose, there is every likelihood of the behavior in the coke oven being affected thereby. Sir J. J. Thomson detected this radioactive gas most readily by its pronounced electrical behavior, and this property would at once ionize the gases in its vicinity and conceivably affect the solid surroundings.

It has been suggested that the corrosion of brickwork has been pronounced where the wash water at the colliery has been used over and over again, thereby becoming heavily charged with soluble salts, but the factor of radioactivity just mentioned may be an equally potent cause.

THE SUGAR INDUSTRY IN CUBA.[*]

It is indeed fortunate for Cuba that the disastrous effects of the European conflict and other conditions upon the tobacco industry of the republic are more than offset by the very material prosperity which the war has brought to the sugar industry, sugar and tobacco being the island's two great staples. The compensation is such that Cuba is today, generally speaking, in a most satisfactory economic condition.

The sugar production of the island in the present year should, with anything like normally favorable weather conditions, exceed greatly any previous crop, as the increase in cane plantings has been enormous. Lands in the western section of the republic that have been idle for 20 years or more, as well as thousands of acres which have been devoted to yucca, bananas, tobacco, and other crops, are this year planted to cane. In the eastern Provinces of Camaguey and Oriente immense tracts of virgin lands have gone under the plow for cane plantings. [Willett & Gray's September 9th estimate of the 1914-15 Cuban sugar yield is 2,600,000 long tons, against a production of 2,597,732 long tons in 1913-14 and 2,428,537 tons in 1912-13.]

Planters and sugar manufacturers have perfect confidence in the continuance of satisfactory prices for a long period, though a few hold pessimistic views as to a possible reaction after the close of the war.

The statistical section of the treasury department of Cuba has recently made public some interesting figures in connection with the sugar industry, and two of the numerous tables contained in its publication, "Industria Azucarera y sus Derivadas," are reproduced below. In Table 1 are given the exports of crude sugar from Cuba and the countries of destination in 1913 and 1914:

TABLE 1.

Sugar and products.	1913 Quantity. Tons.	1913 Value.	1914 Quantity. Tons.	1914 Value.
Crude sugar ...	2,411,188	$122,388,062	2,454,334	$130,413.769
United States	2,129,748	107,975,360	2,164,621	116,479,869
United K'gd'm	240,870	12,598,817	231,541	10,910,416
France	12,077	514,155	26,532	1,433,299
Japan	....	....	19,233	982,124
Canada	23,528	1,088,003	6,724	303,389
Belgium	146	6,500	4,365	223,935
Netherlands .	4,774	204,730	1,154	72,250
	Gallons.		Gallons.	
Molasses	60,982,650	2,027,596	84,652,997	2,445,500
United States.	42,382,685	1,277,025	62,367,741	1,516,937
United K'gd'm.	17,157,409	718,121	20,830,256	884,913
Netherlands .	1,440,000	30,000	1,455,000	43,650
Alcohol	219,478	52,781	173,931	32,684
Aguardiente ...	1,935,546	365,340	1,845,976	325,806
Rum	387,556	95,351	202,336	67,876

The influence of Cuba's sugar industry upon the island's import trade is seen in the large annual purchases of foreign sacks and valuable machinery and apparatus. The imports of these during the past two years are given in Table II:

TABLE II.

Articles and Sources.	1913.	1914.
Bags	$3,059,053	$3,100,916
United States	1,216,490	935,759
British India	1,002,479	1,117,863
United Kingdom	835,394	1,000,796
Mexico	....	32,892
Germany	4,220	13,606
Machinery and apparatus	6,526,030	2,769,904
United States	3,705,975	2,183,430
United Kingdom	921,385	200,375
Belgium	1,068,301	157,172
Germany	592,720	165,910
Netherlands	17,728	50,585
France	216,802	9,127

In connection with the sugar industry it is interesting to note the nationality of the owners of the various sugar estates and mills in the republic. Of the 170 operating estates in the island 67 are owned by Cubans, 43 by Americans, 42 by Spaniards, and 18 by nationals of other countries.

Condensed milk production in the United States exceeds $35,000,000 in value annually, only about 4 per cent of which has been exported.

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[*] From Daily Commerce Reports.

PROPOSED TENTATIVE METHODS FOR THE SAMPLING AND ANALYSIS OF COAL.*

PREPARATION OF LABORATORY SAMPLES.

APPARATUS.

Air-Drying Oven.—The oven is to be used for air-drying wet samples and may be of the form shown in Fig. 1. This is not absolutely necessary but is economical where many wet samples are received.†

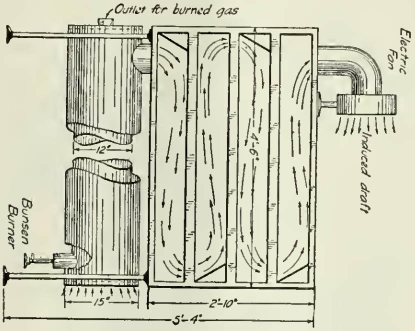

Fig. 1—Dryer for Coarse Samples.

Galvanized-Iron Pans 18 by 18 by 1½ in. Deep.—For air-drying wet samples.

Balance or Solution Scale.—For weighing the galvanized-iron pans with samples. It should have a capacity of 5 kg. and be sensitive to 0.5 g.

Chipmunk Jaw Crusher.—For crushing coarse samples to pass a 4-mesh sieve.

Roll Crusher or Coffee-Mill Type of Grinder.—For reducing the 4-mesh product to 20-mesh. The coffee-mill type of grinder should be entirely enclosed and have an enclosed hopper and a receptacle capable of holding 5 lbs. of coal. This is to reduce the moisture losses while crushing.

Abbé Ball Mill, Planetary Disk Crusher, Chrome-Steel Bucking Board, or any Satisfactory Form of Pulverizer.—For reducing the 20-mesh product to 60-mesh. The porcelain jars for the ball mill should be approximately 9 ins. in diameter and 10 ins. high. The flint pebbles should be smooth, hard and well rounded.

A Large Riffle Sampler, with ½ or ⅝ in. Divisions.—For reducing the 4-mesh sample to 5 lbs. (Fig. 2.).

A Small Riffle Sampler, with ¼ or ⅜ in. Divisions.—For dividing down the 20 and 60-mesh material to a laboratory sample. (Fig. 2.).

An 8-in. 60-mesh Sieve with Cover and Receiver.—Containers for shipment to laboratory. Samples in which the moisture content is important should always be shipped in moisture-tight containers. A galvanized-iron or tin can with a screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit. Samples in which the moisture content is of no importance need no special protection from loss of moisture.

METHOD OF SAMPLING.[1]

(*A*) *When Coal Appears Dry.*

If the sample is coarser than 4-mesh (0.20 in.) and larger in amount than 10 lbs., quickly crush it with the jaw crusher to pass a 4-mesh sieve and reduce it on the larger riffle sample to 10 lbs.[2]; then crush at once to 20-mesh by passing through rolls or an enclosed grinder, and take, without sieving, a 60-g. total moisture sample, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

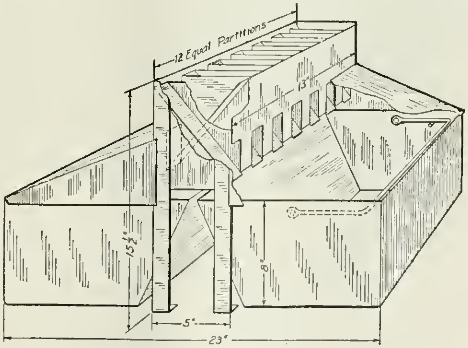

Fig. 2—Riffle Samples.

Thoroughly mix the main portion of the sample, reduce on the small riffle sampler to about 120 g., and pulverize to 60-mesh by any suitable apparatus without regard to loss of moisture. After all the material has been passed through the 60-mesh sieve, mix and divide it on the small riffle sampler to 6^2 g. Transfer the final sample to a 4-oz. rubber-stoppered bottle. Determine moisture in both the 60 and the 20-mesh samples by the method given under moisture.

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*Report of Joint Committee on Coal Analysis of American Society for Testing Materials and the American Chemical Society.

†For details of air-drying oven see Bownocker, Lord and Somermeier, "Coal," Bulletin No. 9, 4th Series, Ohio Geological Survey, p. 312 (1908); or F. M. Stanton and A. C. Fieldner, "Methods of Analyzing Coal and Coke," Technical Paper No. 8, Bureau of Mines, p. 4 (1912); or E. E. Somermeier, "Coal, Its Composition, Analysis, Utilization and Valuation," p. 71. McGraw Hill Book Co. (1912).

[1] Method No. 2 of the preliminary report.

[2] If the sample is crushed to pass a 6-mesh screen it may be reduced to 5 lbs.

Computation.—Compute the analysis of the 60-mesh coal, which has become partly air-dried during sampling, to the dry-coal basis, by dividing each result by 1 minus its content of moisture. Compute the analysis of the coal "as received" from the dry-coal analysis by multiplying by 1 minus the total moisture found in the 20-mesh sample.

(*B*) *When Coal Appears Wet.*

Spread the sample on tared pans, weigh, and air-dry at room temperature, or in the special drying oven, shown in Fig. 1, at 10 to 15° C. above room temperature, and weigh again. The drying should be continued until the loss in weight is not more than 0.1 per cent per hour. Complete the sampling as under dry coal.

Computation.—Correct the moisture found in the 20-mesh, air-dried sample to total moisture "as received," as follows:

$$\frac{100 - \text{percentage of air-drying loss}}{100} \times \text{percentage of moisture in 20-mesh coal} + \text{percentage of air-drying loss} = \text{total moisture "as received."}$$

Compute the analysis to "dry-coal" and "as-re-received" bases as under dry coal, using for the "as-received" computation the total moisture as found by the formula in place of the moisture found in the 20-mesh coal.

NOTES.

Freshly mined or wet coal loses moisture rapidly on exposure to the air of the laboratory, hence the sampling operations between opening the container and taking the 20-mesh total-moisture sample must be conducted with the utmost dispatch and with minimum exposure to air.

The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ more than the following limits:

	Per cent.
No carbonates present	0.4
Considerable carbonate and pyrite present	0.7
Coals with more than 12 per cent ash, containing considerable carbonate and pyrite	1.0

DETERMINATION OF MOISTURE.[3]

APPARATUS.

Moisture Oven.—This must be so constructed as to have a uniform temperature in all parts and a minimum of air space. It may be of the form shown in Fig. 3. Provision must be made for renewing the air in the oven at the rate of two to four times a minute, with the air dried by passing it through concentrated sulphuric acid.

Capsules with Covers.—A convenient form, which allows the ash determination to be made on the same sample, is the Royal Meissen porcelain capsule No. 2, ⅞ in. deep and 1¾ ins. in diameter; or a fused silica capsule of similar shape. This is to be used with a well-fitting flat aluminum cover as shown on page 13 of Technical Paper No. 8, Bureau of Mines.

Glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

METHOD.

(*A*) *Sixty-mesh Sample.*

Heat the empty capsules under the conditions at which the coal is to be dried, stopper or cover, cool over concentrated sulphuric acid, sp. gr. 184, for 30 minutes, and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g. of coal; put this quickly into the capsule close, and weigh at once.

An alternative procedure (more open to error), after transferring an amount slightly in excess of 1 g., is to bring to exactly 1 g. in weight (±0.5 mg.) by quickly removing the excess weight of coal with a spatula. The utmost dispatch must be used in order to minimize the exposure of the coal until the weight is found.

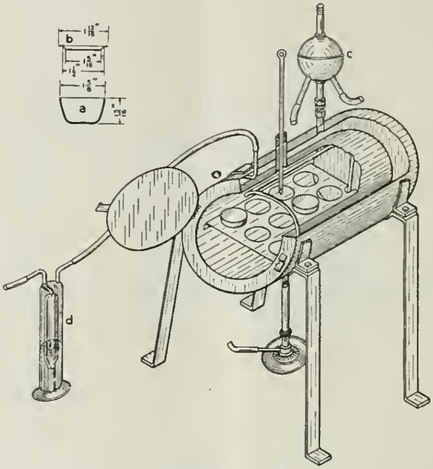

Fig. 3—Toluene or Glycerin and Water Oven for Determining Moisture.

After removing the covers, quickly place the capsules in a pre-heated oven (at 104 to 110° C.) through which passes a current of air dried by concentrated sulphuric acid. Close the oven at once and heat for 1 hour. Then open the oven, cover the capsules quickly and place them in a desiccator over concentrated sulphuric acid. When cool, weigh.

(*B*) *Twenty-mesh Sample.*

Use 5-g. samples, weighed with an accuracy of 2 mg., and heat for 1½ hours; the procedure is otherwise the same as with the 60-mesh sample. Methods of greater accuracy for the determination of moisture are given in the preliminary report.

The allowable variations are as follows:

	Same Analyst, Per cent.	Different Analysts, Per cent.
Moisture under 5 per cent	0.2	0.3
Moisture over 5 per cent	0.3	0.5

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[3] Approximate method of report of Committee D-5 on Standard Specifications for Coal.

DETERMINATION OF VOLATILE MATTER.

APPARATUS.

Platinum Crucible with Tightly Fitting Cover.—The crucible should be of not less than 10 nor more than 20-cc. capacity; of not less than 25 nor more than 35 mm. in diameter; of not less than 30 nor more than 35 mm. in height.

Vertical Electric Tube Furnace; or a Gas or Electrically Heated Muffle Furnace.—The furnace may be of the form as shown in Fig. 4. It is to be regulated to maintain a temperature of 950° C. (±20° C.) in the crucible, as shown by a thermocouple kept in the furnace. A suitable form of electric furnace is shown on page 21 of Technical Paper No. 76, Bureau of Mines. If the determination of volatile matter is not an essential feature of the specifications under which the coal is bought, a Meker burner may be used.

METHOD.

Weigh 1 g. of the coal in a weighed 10 to 20-cc. platinum crucible, close with a capsule cover, and place on platinum or nichrome-wire supports in the furnace chamber, which must be at a temperature of 950° C. (±20° C.). After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, tap the cover lightly to more perfectly seal the crucible and thus guard against the admission of air. After heating exactly 7 minutes, remove the crucible from the furnace, and, without disturbing the cover, allow it to cool. Weigh as soon as cold. The loss of weight minus moisture equals the volatile matter.

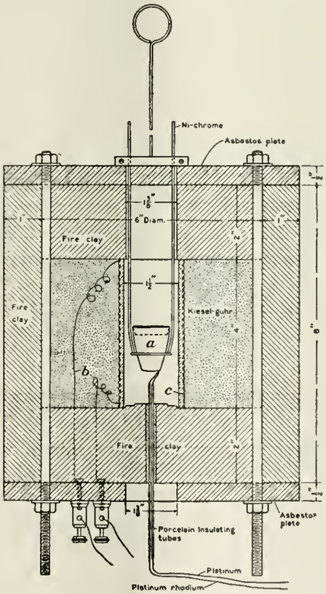

Fig. 4—Electric Tube Furnace for Determining Volatile Matter.

Modification for Sub-Bituminous Coal, Lignite, and Peat.—Mechanical losses are incurred on suddenly heating peat, sub-bituminous coal, and lignite; therefore they must be subjected to a preliminary gradual heating for 5 minutes; this is best done by playing the flame of a burner upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating, transfer the crucible to the volatile-matter furnace and heat for 6 minutes at 950° C. as in the regular method.

The allowable variations are as follows:

	Same Analyst, Per cent.	Different Analysts, Per cent.
Bituminous coals	0.5	1.0
Lignites	1.0	2.0

NOTES.

The cover should fit closely enough so that the carbon deposit from bituminous and lignite coals does not burn away from the under side.

Regulation of temperature to within the prescribed limits is important.

DETERMINATION OF FIXED CARBON AND ASH.

APPARATUS.

Gas or Electric Muffle Furnace.—The muffle should have good air circulation and be capable of having its temperature regulated between 700 and 750° C.

Porcelain Capsules.—Royal Meissen Porcelain Capsules No. 2, ⅞ in. deep and 1¾ in. in diameter, or similar shallow dishes.

METHOD.

Place the porcelain capsules containing the dried coal from the moisture determination in a cold muffle furnace, or on the hearth at a low temperature, and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter. Finish the ignition to constant weight (± 0.001 g.) at a temperature between 700 and 750° C. Cool in air, and weigh as soon as cold. Coals containing carbonate are best cooled in a desiccator.

NOTES.

Before replacing the capsules in the muffle for ignition to constant weight, the ash should be stirred with a platinum or nichrome wire. Stirring once or twice before the first weighing hastens complete ignition.

The result obtained by this method is "uncorrected" ash. For "corrected" ash see the preliminary report. The actual mineral matters in the original coal are usually very different in weight and composition from the weight of the "uncorrected" ash.

The allowable variations are as follows:

	Same Analyst, Per cent.	Different Analysts, Per cent.
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12 per cent of ash, containing carbonates and pyrite	0.5	1.0

Fixed Carbon.—Compute fixed carbon as follows: 100 — (moisture + ash + volatile matter) = percentage of fixed carbon (expressed in percentages).

DETERMINATION OF SULPHUR BY THE ESCHKA METHOD.

APPARATUS.

Gas or Electric Muffle Furnace, or Burners.—For igniting coal with the Eschka mixture and for igniting the barium sulphate.

Porcelain, Silica, or Platinum Crucibles or Capsules.—For igniting coal with the Eschka mixture.

No. 1 Royal Meissen porcelain capsule, 1 in. deep and 2 in. in diameter. This capsule, because of its shallow form, presents more surface for oxidation and is more convenient to handle than the ordinary form of crucible.

No. 1 Royal Berlin porcelain crucibles, shallow form, and platinum crucible of similar size may be used. Somewhat more time is required to burn out the coal, owing to the deeper form, than with the shallow capsules described above.

No. 0 or 00 porcelain crucibles, or platinum, alundum or silica crucibles of similar size are to be used for igniting the barium sulphate.

SOLUTIONS AND REAGENTS.

Barium Chloride.—Dissolve 100 g. of barium chloride in 1,000 c.c. of distilled water.

Saturated Bromine Water.—Add an excess of bromine to 1,000 c.c. of distilled water.

Eschka Mixture.—Thoroughly mix 2 parts (by weight) of light calcined magnesium oxide and 1 part of anhydrous sodium carbonate. Both materials should be as free as possible from sulphur.

Methyl Orange.—Dissolve 0.02 g. in 100 c.c. of hot distilled water and filter.

Hydrochloric Acid.—Mix 500 c.c. of hydrochloric acid, sp. gr. 1.20, and 500 c.c. of distilled water.

Normal Hydrochloric Acid.—Dilute 80 c.c. of hydrochloric acid, sp. gr. 1.20, to 1 liter with distilled water.

Sodium Carbonate.—A saturated solution, approximately 60 g. of crystallized or 22 g. of anhydrous sodium carbonate in 100 c.c. of distilled water.

Sodium-Hydroxide Solution.—Dissolve 100 g. in 1 liter of distilled water. This solution may be used in place of the sodium-carbonate solution.

METHOD.

Preparation of Sample and Mixture.—Thoroughly mix on glazed paper 1 g. of coal and 3 g. of Eschka mixture. Transfer to a No. 1 Royal Meissen porcelain capsule, 1 in. deep and 2 in. in diameter, or a No. 1 Royal Berlin crucible or a platinum crucible of similar size, and cover with about 1 g. of Eschka mixture.

Ignition.—On account of the amount of sulphur contained in artificial gas, it is preferable to heat the crucible over an alcohol flame or in an electrically heated muffle, as in procedure (*a*) following. The use of artificial gas for heating the coal and Eschka mixture is permissible only when the crucibles are heated in a muffle as in procedure (*b*) following.

(*a*) Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of the sulphur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and stirring after all black particles have disappeared, which is an indication of the completeness of the procedure.

(*b*) Place the crucible in a cold gas muffle and gradually raise the temperature to 870-925° C. (cherry-red heat) in about 1 hour. Maintain the maximum temperature for about 1½ hours and then allow the crucible to cool in the muffle.

Subsequent Treatment.—Remove and empty the contents into a 200-c.c. beaker and digest with 100 c.c. of hot water for ½ to ¾ hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash 5 times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 c.c., with 10 to 20 c.c. of saturated bromine water, make slightly acid with hydrochloric acid and boil to expel the liberated bromine. Make just neutral to methyl orange with sodium-hydroxide or sodium-carbonate solution, then add 1 c.c. of normal HCl. Boil again and add slowly from a pipette, with constant stirring, 10 c.c. of a 10 per cent solution of barium chloride ($BaCl_2.2H_2O$). Continue boiling for 15 minutes and allow to stand for at least 2 hours, or preferably over night, at a temperature just below boiling. Filter through an ashless filter paper and wash with hot distilled water until a silver-nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulphate in a weighed platinum, porcelain, silica or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925° C. and heat to constant weight.

The residue of magnesia, etc., after leaching, should be dissolved in hydrochloric acid and tested with great care for sulphur. When an appreciable amount is found this should be determined quantitatively. The amount of sulphur retained is by no means a negligible quantity.[4]

Blanks and Corrections.—In all cases a correction must be applied either (1) by running a blank exactly as described above, using the same amount of all reagents that were employed in the regular determination, or more surely (2) by determining a known amount of sulphate added to a solution of the reagents after these have been put through the prescribed series of operations. If this latter procedure is adopted and carried out, say, once a week or whenever a new supply of a reagent must be used, and for a series of solutions covering the range of sulphur content likely to be met with in coals, it is only necessary to add to or subtract from the weight of barium sulphate obtained from a coal, whatever deficiency or excess may have been found in the appropriate "check" in order to obtain a result that is more certain to be correct than if a "blank" correction as determined by the former procedure is applied. This is due to the fact that the solubility error for barium sulphate, for the amounts of sulphur in question and the conditions of precipitation prescribed, is probably the largest one to be considered. Barium sulphate is soluble[5] in acids and even in pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, in the event of using reagents of very superior quality or of exercising more than ordinary precautions, there may be no apparent "blank," because the solubility limit of the solution for barium sulphate has not been reached or at any rate not exceeded.

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[4] Journal, Am. Chem. Soc., Vol. 21, p. 1125 (1899).

As shown in the preliminary report,[6] the Atkinson and sodium-peroxide methods give results in close agreement with the Eschka method. Register[7] has shown that if 5 per cent of nitrogen is present in the gases contained in the bomb calorimeter the sulphur of a coal is almost completely oxidized to sulphuric acid and the washings of the calorimeter may be used for the determination of sulphur.

DETERMINATION OF PHOSPHORUS IN ASH.

Method No. 1. To Cover All Cases.—To the ash from 5 g. of coal in a platinum capsule is added 10 c.c. of nitric acid and 3 to 5 c.c. of hydrofluoric acid. The liquid is evaporated and the residue fused with 3 g. of sodium carbonate. If unburned carbon is present 0.2 g. of sodium nitrate is mixed with the carbonate. The melt is leached with water and the solution filtered. The residue is ignited, fused with sodium carbonate alone, the melt leached and the solution filtered. The combined filtrates, held in a flask, are just acidified with nitric acid and concentrated to a volume of 100 c.c. To the solution, brought to a temperature of 85° C., is added 50 c.c. of molybdate solution and the flask is shaken for 10 minutes. The precipitate is washed six times, or until free from acid, with a 2 per cent solution of potassium nitrate, then returned to the flask and titrated with standard sodium hydroxide solution. The alkali solution may well be made equal to 0.00025 g. phosphorus per cubic centimeter, or 0.0005 per cent for a 5-g. sample of coal, and is 0.995 of one-fifth normal.[8] Or the phosphorus in the precipitate is determined by reduction and titration of the molybdenum with permanganate.

Note on Method No. 1.—The advantage of the use of hydrofluoric acid in the initial attack of the ash lies in the resulting removal of silica. Fusion with alkali carbonate is necessary for the elimination of titanium, which if present and not removed will contaminate the phospho-molybdate and is said to sometimes retard its precipitation.

Method No. 2.—When titanium is so low as to offer no objection, the ash is decomposed as under method No. 1, but evaporation is carried only to a volume of about 5 c.c. The solution is diluted with water to 30 c.c., boiled, and filtered. If the washings are turbid they are passed again through the filter. The residue is ignited in a platinum crucible, fused with a little sodium carbonate, the melt dissolved in nitric acid and its solution, if clear, added to the main one. If not clear it is filtered. The subsequent procedure is as under method No. 1. The fusion of the residue may be dispensed with in routine work on a given coal if it is certain that it is free from phosphorus.

ULTIMATE ANALYSIS.

For Methods of Ultimate Analysis, see Vol. XIV, Part I, of the *Proceedings*, p. 436.

CALORIMETRIC DETERMINATION.

APPARATUS.

Combustion Bombs.—The Atwater, Davis, Emerson, Mahler, Parr, Peters, Williams, or similar bombs may be used. The bomb shall have an inner surface of platinum, gold, porcelain enamel, or other material which is not attacked by nitric and sulphuric acids, or other products of combustion.

Calorimeter Jacket.—The calorimeter must be provided with a water-jacket having a cover to protect the calorimeter from air currents. The jacket must be kept filled with water within 2 or 3° C. of the temperature of the room (except in calorimeters which are totally submerged, where the jacket temperature is controlled by a thermostat) and should be stirred continuously by some mechanical stirring device.

Stirring of the Calorimeter Water.—The water in the calorimeter must be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. A motor-driven screw or turbine stirrer is recommended and the speed should not be excessive. This may be determined by adjusting the temperature of the calorimeter to equality with that of the jacket and allowing the stirrer to run continuously for ten minutes. If the temperature of the calorimeter rises more than about 0°.01 C. in this length of time, the rate of stirring is excessive. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is irregular. The portion of the stirring device immersed in the calorimeter should be separated from the outside by non-conducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

Thermometers.—Thermometers used shall have been certified by a government testing bureau and shall be used with the corrections given on the certificate. This shall also apply to electrical resistance or thermo-electric thermometers. Correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the "setting" of Beckmann thermometers. For accurate work, either Beckmann or special calorimetric thermometers graduated to 0.01 or 0°.02 C. are required. Such thermometers should be tapped lightly just before each reading to avoid errors caused by the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it up with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

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[5] Journal, Am. Chem. Soc., Vol. 32, p. 588 (1910); Vol. 33, p. 829 (1911).

[6] Journal of Industrial and Engineering Chemistry, Vol. 5, p. 5 (1913).

[7] Ibid., b., p. 812 (1914).

[8] Ulmann and Buch, Chemical Engineer, Vol. 10, p. 130 (1909).

Oxygen.—The oxygen used for combustions shall be free from combustible material. The bomb when filled should contain at least 5 per cent of nitrogen to insure complete oxidation of the sulphur.[9] The total amount of oxygen contained in the bomb for a combustion shall not be less than 5 g. per gram of coal. But the combustion must be complete, as shown by the absence of any sooty deposit on opening the bomb after firing.

Firing Wire.—The coal in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used, it should be of about No. 34 B. & S. gage and not more than 10 cm. (preferably 5 cm.) should be used at a time. A correction of 1,600 calories per gram weight of iron wire burned is to be subtracted from the observed number of calories.

Standardization.—The water equivalent of a calorimeter can best be determined by the use of the standard combustion samples supplied by the Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of standard samples supplied by the Bureau of Standards, and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of either the same or different standard materials. The conditions as to the amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made shall be the same as for coal combustions. In the case of any disagreement between contracting parties a check standardization may consist of two or more combustions of standardizing samples.

MANIPULATION.

1. *Preparation of Sample.*—The ground sample is to be thoroughly mixed in the bottle and an amount, approximately 1 g., is to be taken out and weighed in the crucible in which it is to be burned. Coals which are likely to be blown out of the crucible should be briquetted. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation in the use of naphthalene for standardization.

2. *Preparation of the Bomb.*—The firing wire, if iron, should be measured and coiled in a small spiral and connected between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron must both be clean. About 0.5 c.c. of water should be placed in the bottom of the bomb to saturate with moisture the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the coal or briquette of standard material. For the combustion of standardizing samples iron wire is preferable to platinum.

3. *Filling the Bomb with Oxygen.*—Oxygen from the supply tank is to be admitted slowly to avoid blowing the coal from the crucible, and the pressure allowed to reach 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs, so that the bomb shall contain an amount of oxygen sufficient for complete combustion, namely, at least 5 g. per gram of coal, or other combustible. This method of filling will insure 4 per cent of nitrogen in the larger bombs, irrespective of the nitrogen contained in the oxygen.

4. *Calorimeter Water.*—The calorimeter is to be filled with the required amount of distilled water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standardized flask or by weighing. The amount must be kept the same as that used in standardization of the apparatus.

5. *Temperature Adjustments.*—The initial temperture in the calorimeter should be so adjusted that the final temperature, after the combustion, will not be more than 1° C., preferably about 0°.5 C., above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be small when the rise of temperature is 2 or 3° C. and the effect of evaporation will also be small.

6. *Firing Current.*—The electric current used for firing the charge should be obtained from storage or dry cells having an electro-motive force of not more than 12 volts, since a higher voltage is liable to cause an arc between the firing terminals, introducing additional heat, which cannot be measured with certainty. The circuit should be closed by means of a switch which should remain closed for not more than 2 seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out.

7. *Method of Making an Observation.*—The bomb when ready for firing, is to be placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer is then started and after the thermometer reading has become steady, not less than 2 minutes after the stirrer is started, temperatures are read at 1-minute intervals for 5 minutes and the charge is then fired, the exact time of firing being noted. Observations of temperature are then made at intervals depending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings is taken at 1-minute intervals for 5 minutes to determine the final cooling rate.

8. *Titration.*—After a combustion the bomb is to be opened, after allowing the gas to escape, and the inside examined for traces of unburned material or sooty

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[9] Cf. Register, Journal of Industrial and Engineering Chemistry, Vol. 16, p. 812 (1914).

deposit. If these are found, the observations shall be discarded. If the combustion appears complete, the bomb is to be rinsed out thoroughly and the washings titrated with a standard alkali solution (1 c.c. = 0.2173 g. HNO_3 = 5 calories) using methyl-orange or methyl-red indicator, to determine the amount of acid formed. A correction of 230 calories per gram of nitric acid should be subtracted from the total heat observed. An additional correction of 1,300 calories per gram of sulphur in the coal should be made for the excess of difference in heats of formation of SO_2 and aqueous H_2SO_4 over the heat of formation of aqueous HNO_3.

COMPUTATION OF RESULTS.

The following method of computation is recommended to take the place of the Pfaundler or other similar formulas for computing the cooling correction (radiation correction).

Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for 5 minutes before firing; (2) the time (a) at which the last temperature reading is made immediately before firing; (3) the time (b) when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing, 60 per cent of the expected[10] temperature rise, and noting the time when this point is reached); (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some 5 minutes after firing; (5) the final rate of cooling (r_2) in degrees per minute for 5 minutes.

The rate r_1 is to be multiplied by the time $b - a$ in minutes and tenths of a minute, and this product added (subtracted if the temperature was *falling* at the time a) to the thermometer reading taken at the time a. The rate r_2 is to be multiplied by the time $c - b$ and this product added (subtracted if the temperature was *rising* at the time c and later) to the thermometer reading taken at the time c. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated. This result, corrected for the heats of formation of HNO_3 and H_2SO_4 observed and for the heat of combustion of the firing wire, when that is included, is to be divided by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the British thermal units per pound. (See example.)

In practice, the time $b—a$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

The results should be reduced to calories per gram or British thermal units per pound of *dry coal,* the moisture being determined upon a sample taken from the bottle at about the same time as the combustion sample is taken.

EXAMPLE.

OBSERVATIONS.

Water equivalent = 2550 g.
Weight of charge = 1.0535 g.
Approximate rise of temperature expected = 3°.2.
60 per cent of approximate rise = 1°.9.

Time.	Thermometer Readings.	Corrected Temperature (or corrected Beckmann thermometer readings).
10-21	15° .244	Thermometer corrections taken from the certificate.
22	.250	
23	.255	
24	.261	
25	.266	
(*a*) 26	.272	15° .276
	Charge fired	
(*b*) 27.2	17° .2[d]	18° .497
31	18° .500	
32	.498	
33	.497	
34	.498	
35	.494	
36	.493	

COMPUTATION.

$r_1 = 0°.028 \div 5 = 0°.0056$ per minute. $b—a = 1.2$ minutes.
The corrected initial temperature is
$15°.276 + 0°.0056 \times 1.2 = 15°.283$.
$r_2 = 0°.007 \div 5 = 0°.0014$ per minute; $c—b = 3.8$ minutes.
The corrected final temperature is

18° .497 + 0.0014 × 3.8	= 18° .502	
Total rise 18° .502 — 15° .283..............	= 3° .219	
Total calories 2550 × 3.219................	=	8209
Titration, etc.		—7
Calories from 1.0535 g. coal..............		8202
Calories per gram........................	7,785	
or British thermal units per pound........	14,013	

[d] The initial temperature is 15°.27; 60 per cent of the expected rise is 1°.9. The reading to observe is then 17°.2.

The result obtained by the above method of computation and determination is the total heat of combustion at constant volume, with the water in the products of combustion condensed to liquid at the temperature of the calorimeter, that is, about 20 to 35° C.

Net heat of combustion at 20°, shall refer to results corrected for latent heat of vaporization, as follows:

Total heat of combustion in B. t. u. — 1,040 (hydrogen × 9) = net heat of combustion in B. t. u. per pound.

Also

Total heat of combustion in calories — 580 (hydrogen × 9) = net heat of combustion in calories per gram.

NOTES.

For anthracite, coke and coal of high ash content, which do not readily burn completely, the following procedure is recommended:

The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles. The coal is then sprinkled evenly over the surface of the asbestos. Otherwise the procedure is as previously described.

The method of computing the "cooling correction" described in Technical Paper No. 8, Bureau of Mines, pages 28 to 32, may also be used.

ALLOWABLE VARIATIONS.

	Per cent.
Same analyst	0.3
Different analysts	0.5

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[10] When the temperature rise is not approximately known beforehand, it is only necessary to take thermometer readings at 40, 50, 60 seconds (and possibly 70 seconds with some calorimeters) after firing, and from these observations to find when the temperature rise had reached 60 per cent of the total. Thus, if the temperature at firing was 2°.135, at 40 seconds 3°.05, at 50 seconds 3°.92, at 60 seconds 4°.16, and the final temperature was 4°.200, the total rise was 2°.07; 60 per cent of it was 1°.24. The temperature to be observed was then 2°.14+1°.24=3°.38. Referring to the observations at 40 and 50 seconds, the temperatures were respectively 3°.05 and 3°.92. The time corresponding to the temperature of 3°.38 was therefore

$$40 + \frac{3.38 - 3.05}{3.92 - 3.05} \times 10 = 44 \text{ seconds.}$$

PAPER FIBER ANALYSIS.*

By MAX CLINE.†

The manufacturer of the ordinary grade of paper finds that his business is becoming highly competitive, with production increasing faster than the demand. Often he finds that he has to change his production from one grade to another in order to run at a profit. It is very important for him to know, as exactly as possible, the composition of the various grades of paper on the market which he might be able to manufacture.

The mechanical qualities of some of the papers, through years of progressive manufacture, are remarkably high for their market value, and that such papers can be made from the stock found in them seems impossible, until a careful study is made as to correction of stock and mechanical adjustments in the plant. Being certain of the stock composition of the paper he desires to make, the manufacturer can devote his entire attention to making the plant adjustments necessary to meet his problem.

Uncertainty in the stock composition of the paper complicates the problem; moreover every 1 per cent replacement of unbleached sulphite by groundwood means a saving of 20c a ton, the same change for bleached stock effecting a saving of 40c a ton; while a replacement of 5 per cent might make the whole difference as to profit or loss in the manufacture of that particular paper.

In the hands of the skillful manufacturer, groundwood has changed from the simple wood filler of former days to the flexible product of the present. By wood selection, variation in grinding, in screening, in bleaching, the quality of the mechanical pulp is greatly modified so that it answers a variety of purposes in changing the quality of the paper in which it is furnished, with the result that it is going more and more into grades of paper deemed impossible years ago.

It is of the utmost importance for the manufacturer of the cheaper grades of paper to know what can be done with groundwood, and he is not fully informed until he has had submitted to him careful analyses of the paper made by his competitors.

The consumer of paper still holds to the old prejudice of regarding groundwood as a necessary evil—an ingredient to be furnished in his paper only to the extent of lowering his own costs. He fails to understand, or forgets often, that certain highly desirable qualities as to formation, feel, and finish, in his paper can only be attained by the liberal use of groundwood, and that to substitute other stock for groundwood to give him the qualities of the paper demanded would make the cost prohibitive.

When the quality of the paper does not come up to expectation he is inclined to be too ready to jump to the conclusion that a greater furnish of groundwood in the paper was made than he specified. To verify his suspicion he submits a sample of the paper to his chemist or consulting chemist for analysis, and it is of the gravest importance to all concerned that this work be done with as great accuracy as our present scientific knowledge will permit.

What then can the paper mill chemist or the consulting chemist do to meet this want of the manufacturer or consumer of paper?

As an illustration let us take a recent case of the fiber analysis of two samples of paper by four laboratories:

	Sample 1 Groundwood Per cent.	Sample 2 Groundwood Per cent.
Laboratory A	50	45
Laboratory B	31	29
Laboratory C	35	40
Laboratory D	30	25

Showing a maximal variation of 40 per cent in the analyses.

Only two, B and D, check each other fairly well on both samples, C checks B and D on sample 1, and A on sample 2. Considering that one laboratory is of national prominence as catering to the pulp and paper trade, that another is that of a large manufacturer of groundwood papers with considerable experience in the analysis of such papers; a third, the paper laboratory of a large dyestuffs concern, composed of men having a considerable training in fiber analysis; and a fourth, that of men having an international reputation as cellulose experts, it seems that they should all have agreed quite closely. No doubt, under present conditions, most analysts would not agree more closely on fiber determination than A B C or A C D.

Two questions arise. Is this the best that can be expected, and if not not, should we remain satisfied with poor work? In answering these questions let us briefly examine the methods available for groundwood determinations in paper.

Broadly the methods divide themselves into three general procedures:

(1) Color reactions due to staining of the paper with reagents of which the most preferred are phloroglucinol, aniline sulphate and dimethyl-para-phenylenediamine.

(2) Microchemical examination of the fibers with the help of staining solutions, such as iodine or iodo-zinc-chlor solution.

(3) Chemical procedures, such as the determination of the phloroglucinol absorption number or the cellulose determination of the sample in question.

The first, or staining, method of the sample of paper with reagents is very useful as a qualitative test for the presence of groundwood in papers containing bleached or well cooked wood celluloses. When there is a possibility of the presence of lignified wood cellulose, such as rather raw unbleached sulphite or kraft pulp, this test should be confirmed by microscopical examination.

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*From a paper read Sept. 23, 1915, before the Technical Section of the American Paper and Pulp Association.

†Chemist, Bureau of Tests, International Paper Company, Glens Falls, N. Y.

Superficial staining of paper, such as Wurster's color reactions, has been proposed for the quantitative determination of groundwood, and to make the procedure more simple and rapid, color charts are offered to the paper analyst with the advice that all he has to do is to put a drop of the reagent on the sample he is examining and compare with chart. This may be satisfactory for ideal mixtures of stock of ideal quality, but the result in practice is about as happy as comparing the average person with the fashion plates as pictured in the popular magazines.

A moment's consideration will show that the depth of stain depends on the quality of the reagent and its age, the time in which the reagent is allowed to act, and the quality of the different pulps in the paper, besides the per cent composition of the same. It is hopeless even to expect a crude approximation of the percentage of groundwood to be determined in paper by this method unless the analyst makes a series of hand samples of paper containing varying amounts of groundwood and wood celluloses of as near the quality contained in the sample as possible.

The examiner will also find that the variation in the depth of stain developed by varying quantities of groundwood is not delicate enough for papers containing large amounts of groundwood. At the best the quantitative results are highly unsatisfactory and as a microscope has to be used anyway, it is just as well to employ a microchemical method in the first place and get much more satisfactory results.

This leads us to the second or microchemical method for the determination of groundwood in paper. It is needless to go into a description of the procedure or of the stains that are used. Every book on papermaking repeats the procedure and a few enter into lengthy descriptions of microchemical analysis of fiber.

The whole procedure appears very simple, the amount of skill required for the manipulation of the microscope for fiber analysis being so slight that even the rawest tyro at analytical work faces the task boldly. So charmingly easy does microchemical analysis of fiber appear that the operator forgets or overlooks the quiet observation of the cellulose experts, embraced in the remark that "the degree of accuracy attainable depends first upon the kind of mixture under examination, and secondly, upon the experience of the observer."

Many a laboratory considers the procedure too simple for an analyst to take time to prepare fiber slides for examination and leaves it to a laboratory helper. As some laboratory helpers are not strongly imbued with the chemist's regard for analytical cleanliness, a boomerang occasionally leaves such a laboratory in a report on a certain percentage of rag stock in paper made at a mill that never lifted its eyes above unbleached sulphite. Nor does the suggestion from some kind friend that possibly the beaterman lost his overalls or handkerchief in the engine help the embarrassed laboratory.

Another pitfall that a laboratory may and often does get into, is to have its whole force or a good part of it pass judgment on a fiber analysis by microchemical examination. This is based on the theory that the voice of the multitude is righteous and the opinion of the many is correct. Unfortunately this does not work out in practice.

Whether in politics or microchemical fiber analysis, the average opinion of mere numbers is not necessarily correct or accurate, especially if it has within itself the judgment of the careless, the thoughtless, and the unprepared. To ask a man who is, let us say, engaged in a carbon determination on a sample of steel, or who is analyzing a bronze, to drop his work as soon as convenient and spend a few minutes in examining one or more fiber slides and to record his vote is not fair to the subject. This man may not have seen a fiber slide in two days or even a week. His mind is, or ought to be, charged with the work which occupies most of his time. He will approach the microscope with a clouded vision and will neglect the many niceties which are vital for careful work.

He will take it for granted that the sample was defiberized properly and that the microscopic slide, or slides, gives a correct picture of the average fiber composition of the sample, which, as already noted, sometimes leads to very absurd reports. He may overlook the point that the stain is not working properly, that the fields vary greatly in composition and he may be too impatient to examine a large enough number of fields to get an accurate analysis. Or if the observer is conscientious enough to examine known standards for comparison, he may neglect to note that some allowance should be made for the variation in treatment of the stock in the unknown from the standards, or that the comparison is not exactly fair, as the unknown may contain rather raw sulphite with groundwood, while the standards are made up of mixtures of well cooked unbleached sulphite and groundwood. Inexperienced men will obtain wide variations in test results, and a sample may be reported as containing 25, 50 or 75 per cent groundwood, or *about* 25, 50 or 75 per cent groundwood. This may account for men often checking each other quite well and still be far from strict accuracy of determination.

As a rule, the opinion of one thoroughly trained, patient and thoughtful fiber analyst is more correct after, let us say, half an hour's work on a microchemical fiber examination than the average judgment of six inexpert men who have collectively spent three hours on the test.

Another fallacy peculiar to analysts is to report percentage of stock by counting the fibers. A moment's consideration will show that this can only hold true if the groundwood contain just as many fibers, shreds of fiber, and bundles of fiber per pound of stock as the cellulose contained fibers and parts of fiber and that it is absurd to expect such close agreement in pulps so utterly unlike in composition and method or preparation as groundwood and the celluloses.

I hope that I have shown you that consistent accuracy in microchemical fiber analysis is far from easy—that it requires experience, patience and good judgment; that a large number of standards made from paper similar to those under investigation should be employed, i. e., standards made up of the same quality cellulose pulp which had been treated and refined in as near the same way as the stock in the unknown sample.

Microchemical fiber analysis is very rapid, and it is this which makes it so popular for groundwork determinations, but it is in reality much more difficult to get accurate results by this method than by the more complicated and more time-consuming chemical methods.

The chemical methods take cognizance of the fact that groundwood or mechanical woodpulp is altogether different from the wood celluloses or any other cellulose, being composed of the complicated lignocellulose and so reacts chemically different.

The phloroglucinol absorption method first proposed by Cross, Bevan and Sindall was found by us to be a very useful and accurate procedure for groundwood determinations. It is true that it takes at least fifteen hours to get the result; the titration of excess phloroglucinol with formaldehyde is rather tedious and the reagent has to be freshly prepared for each test, as it does not keep well. Furthermore, in accurate work, the absorption number of the stock with which the sample paper was made should be determined at the same time, or, failing that, the absorption number of standard pulps, of as near the same lignin content as the stock in the sample, should be found. It is also necessary to determine the nonfibrous constituents of the sample.

The analyst who takes these precautions is well rewarded for his pains. The greatest accuracy of the microchemical methods is easily excelled by this method. Accuracy to 1 and 2 per cent groundwood is often obtained in simple mixtures of two pulps. At the Bureau of Tests, of the International Paper Company, we have the opportunity of testing this method on paper of known furnish of mixtures of groundwood and sulphite and are well satisfied with its consistent accuracy.

Another chemical method that is applicable and gives good results is to determine the cellulose content of the sample by any good method such as the chlorination method. By determining the cellulose content of the mechanical woodpulp and the chemical woodpulps we obtain a proportion from which the percentage of groundwood in the sample may be calculated. This method has been found to check the phloroglucinol method very well in the few cases we have tried it in using both methods.

As an example we recently analyzed a sample of paper which had a phloroglucinol absorption number of 3.4, the groundwood from which it was made gave 7.2 and the unbleached sulphite 1.8; this gives us 29.6 per cent groundwood on the bone-dry, ash-free, size-free basis. At the same time we found that the sample contained 76.2 per cent cellulose, the groundwood pulp 55.7 per cent, and the unbleached sulphite 84.5 per cent, which gives us 29.0 per cent groundwood.

With such possibilities from the chemical methods it is not reasonable for analysts to rely entirely on the microchemical method, as many now do. Where quick results are wanted and an approximate determination satisfactory, the microchemical method can be used exclusively. But where accuracy is the aim no pains should be avoided to make the analysis as careful as possible.

It would be useful for the Technical Section of the American Paper and Pulp Association to adopt a standard method for fiber determination and thus avoid the existing confusion and sources of dispute in the trade.

A bibliography of the chemistry of gas manufacture has just been issued by the United States Bureau of Mines. The references in this bibliography are selected from a much larger list, gathered by the Bureau during several years of research work on problems dealing with the chemical behavior of hydrocarbons. No attempt is made to cover every phase of gas manufacture, including the construction and operation of plants, the object being to present a bibliography of carefully chosen references dealing with the chemistry of gas making and the chemical changes involved in the production of combustible gases. In view of the fact that there is no such published bibliography, the list, together with its cross references, is published by the Bureau of Mines in the hope that it will serve as an efficient guide for investigators, chemists and engineers, and for operators of gas plants. Copies of this document, Technical Paper 120, may be obtained by addressing the Bureau of Mines, Washington, D. C.

It is reported from Bucharest that the total production of petroleum in Roumania during the first half of 1915 amounted to 906,472 tons, as compared with 878,516 tons for the first half of 1914. Of the total for the first half of 1915 the district of Prahova contributed 87.79 per cent, Dombovida 5.77 per cent and Buzare 4.83 per cent.

The low price of silver has not noticeably lessened mining and development in the Cobalt camp, says the Canadian Government Labor Gazette. The price of silver, which it mentioned as 47 cts. per ounce, has since gone up, and is now about 50.6 cts.

METALLURGY

TREATMENT OF SILVER FURNACE FUME BY THE COTTRELL PROCESS.*

By **CHARLES H. ALDRICH.**

The problem of condensation or agglomeration of the very minute particles constituting metallurgical fume has, until within recent years, furnished a problem very difficult of solution. It is, however, in many cases, extremely important, both as to its bearing upon the health of the community and upon the valuable products which may be recovered by the operation.

In the past, many tons of valuable materials have been lost through volatilization and dissipation with furnace gases, and, although the subject of metallurgical fume has received a great deal of attention of late, yet there is no doubt that in many instances fume losses are occurring daily that are entirely unsuspected by those in charge of the operations.

It has often been assumed that because the dust deposited at the end of a long flue system amounts to very little, no large amount of values pass out of the stack, and the important points that fume as well as dust may carry large values and that they present problems that demand individual treatment, are lost sight of.

During the past four years considerable work has been done at the Raritan Copper Works on treatment of gases from Doré refining furnaces, and we believe that we are in a position to state that the problem of the recovery of practically all metal values from these gases has been solved by the application of the Cottrell process.

Since this plant was the first one to use this process in connection with silver refining, a description of the methods used and results obtained will, perhaps, be of interest.

Prior to the year 1907 the only method in use for recovering values from silver furnace gases was a system of brick flues, about 12 square feet (1 sq. m.) in cross section and 250 feet (75 m.) long, leading to a brick stack 90 feet (27 m.) high.

When a large addition to the plant was constructed in 1906, the silver refinery was remodeled and enlarged, and it was decided to install a water scrubber on the end of the flue system, based on results obtained at the Baltimore Copper Smelting and Rolling Co. with a similar apparatus. This consisted of a lead-lined tank filled with water, into which dipped 336 5-inch (13 cm.) lead pipes, which projected about 5 inches (13 cm.) below the surface and communicated with a cast-iron gas chamber above. The furnace gases were drawn from the flues by means of a six-foot (1.8 m.) centrifugal blower and forced through the pipes, bubbling through the water and passing out of a lead stack connected to one end of the tank.

The results obtained with this apparatus amply justified the considerable expense involved in its installation and maintenance, and during its operation it has saved values averaging about $50.00 per day.

It seemed evident, both from the appearance of the gases passing out and from the nature of the treatment, that no dust could be escaping, and for some time it was thought that no values of importance were being lost; the escaping cloud being apparently mostly steam. However, it was observed that if a metal sheet was suspended in the gases a deposit would form upon it which often carried several hundred ounces of silver per ton.

Early in 1911 tests were started to determine the advisability of constructing a settling flue through which the gases could be passed after leaving the scrubber and not until then was the true nature of the fume or the importance of its recovery realized.

It was found that, as had been supposed, practically all dust had been removed from the gases by the scrubber, the material remaining all being in the form of particles so fine that they formed a fog, which when placed in a closed vessel, required from two and a half to three hours to clear up. Obviously, no practical settling flue could be constructed to accomplish this. Violent agitation with water, it was found, would clear up the gas. Accordingly, the installation of various mechanical gas-washers was considered. The problem of acid proofing appeared serious, and, as these gases contained large proportions of nitric and sulphuric acids, it will be seen that this was of importance.

A device in which the gases were to be forced through a series of lead screens in contact with running water appeared to be the most practical, and some working drawings of this were made. There were many points about this, however, which were not satisfactory. Consequently, when Dr. Cottrell's paper upon "The Electrical Precipitation of Suspended Particles" appeared in the *Journal of Industrial and Engineering Chemistry*, August, 1911, it seemed likely that the process described would perhaps accomplish the desired result upon our gases. Dr. Cottrell was communicated with and shortly after arrangements were made with him to conduct tests, and, if favorable results were obtained, to construct a treater of sufficient capacity to handle the gases.

Electrical apparatus for converting 220-volt direct current up to about 45,000 volt D. C. was obtained, and during the summer of 1912 a series of tests were conducted by Mr. Linn Bradley, representing the Research Corporation, and the writer, which gave such encouraging results that it was decided to go ahead with the construction of the treater.

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*Paper presented at the 28th general meeting of the American Electrochemical Society, in San Francisco, in Joint Session with the American Institute of Electrical Engineers, Sept. 17, 1915.

With regard to the details of these tests, little need be said. Briefly, the method used was the aspiration of a definite proportion of the gases, measured by a Pitot tube, through a treater composed of a 10-foot (3 m.) length of 6-inch (5 cm.) pipe provided with a central electrode of No. 20 (0.8 mm.) copper or iron wire. Clearance was determined by aspirating equal volumes of gases simultaneously through Brady filters, located at the inlet and outlet ends of the treater pipe, and assaying the filter thimbles for silver and gold.

The electrical apparatus used in the preliminary work was far from practical. It was designed for X-ray work and included a multiplicity of condensers and inductance coils together with a transformer impregnated with beeswax but without provision for cooling; consequently, as might be expected, a large proportion of time was occupied in repairing punctured condenser plates and scooping up the beeswax that ran out of the transformer.

The electrical apparatus finally secured for the commercial treater, which has now been running continuously for nearly two years, consisted of a 3-k.w., 220-volt, d. c., to 154-volt a. c., 60 cycle, "Hill" rotary converter, a 7.5-k.w. 154-50,000-volt, American Transformer Co. oil-cooled transformer, and a rotary rectifying switch, designed jointly by the Research Corporation and the Raritan Copper Works. Shortly after starting the commercial treater, on account of experiences at some other plants, air choke-coils were placed in circuit with the high-tension terminals of the transformer to protect the windings from puncture caused by excessive voltages due to surges.

At that time the plate treater was considered the most practical for our work, and designs were made along these lines. It was decided to use cast-iron as far as possible in the construction, but the question of the most suitable material to use for discharge wires furnished a perplexing problem. The gases were extremely corrosive, and tests made on wires of iron, steel, nickel, monel metal, aluminum and various copper alloys, proved all to be unsatisfactory. Tungsten wire was tried and found to stand up very well, but, on account of its cost and stiffness it did not seem practical. The solution of the problem was the employment of lead strips, one inch (2.5 cm.) wide, sharpened on the edges and set transversely between each pair of collecting plates. These have been perfectly satisfactory, the original strips still being in use.

The treater, as constructed, consisted of a rectangular cast-iron chamber, 8 ft. (2.4 m.) wide by 6 ft. (1.8 m.) high by 16 ft. (4.8 m.) long, set over a lead-lined hopper connecting with a sludge tank through a launder. Collecting electrodes, consisting of 6-inch (15 cm.) lead strips, were hung parallel with the gas flow, through cast-iron bars which also carried the cover plates. The lower ends of the strips were guided by slotted iron bars resting on flanges cast on the lower edges of the frame end plates. Cast-iron I-beams, carried on each side of the treater on high tension pedestal insulators, formed the high tension bus bars, and these carried four cast-iron channels running transversely through openings in the sides of the treater, which supported the discharge electrode frames. It was thought likely that considerable trouble would be experienced with discharge electrodes breaking, and, to provide for easy repairs, these electrodes were set in rectangular cast-iron frames provided with lugs on each side of the top, the whole thing being thereby supported on two of the transverse channels. A cover was placed over each of these electrode frames so that, by simply lifting off the cover, the frame beneath running half the length of the treater was easily accessible and could be lifted out bodily, if necessary.

As to durability, cast iron has proved very satisfactory in the sides and top; however, wherever there has been an intense electrical discharge, as from the discharge electrode frames, the iron has been quickly corroded. Lead, however, has proved entirely satisfactory under all conditions, and all iron discharge frames and guide bars have been replaced by lead-covered wrought iron.

In our opinion, the gases leaving the Doré furnaces pass first into a four-foot (1.2 m.) diameter, sheet-iron flue about 40 feet (12 m.) long, then into a brick flue 6 ft. (1.8 m.) wide by 7 ft. 6 in. (2.3 m.) by 80 ft. (24 m.) long. A centrifugal fan, operated by a 40-h.p. motor, is placed on the end of this flue. This draws the gases out and forces them through iron connecting flues tangentially into the base of a circular brick settling chamber, 16 ft. (4.8 m.) in diameter by 17 ft. (5.1 m.) high. The whirling motion imparted to the gases in this chamber assists materially in depositing the particles of dust. An iron flue, 3 feet (0.9 m.) in diameter, leads from the center of the top of this chamber into a horizontal brick flue, which, in turn, opens into the scrubbers, the treater being connected to the scrubber outlet.

It will thus be seen that enough settling is secured in this system to remove practically all the values that are present in the form of dust, before the treater is reached; the only material passing to the treater being true fume. The flue and scrubber system are the same as were in use before the treater was built, consequently, the values which have been recovered by the treater would have been lost under former conditions.

The average analysis of the dust deposited in the treater is as follows:

	Per cent.
Selenium	6.5
Tellurium	6.0
Arsenic	10.0
Antimony	28.0

Lead	9.0
Bismuth	2.0
Copper	0.9
Silver	800 oz. per ton
Gold	1 oz. per ton

The total recovery averages 29.2 per cent of the silver and 6.6 per cent of the gold caught in the whole flue dust system.

Of the total amount treated in the furnaces, this is 0.24 per cent of the silver and 0.022 per cent of the gold.

All elements are highly oxidized, and silver and gold are combined with the base metals present in extremely insoluble forms, all attempts to remove them by acid treatment having been unsuccessful. It is also interesting to note that the silver in treater sludge runs about twice as high as in scrubber sludge. Gold runs about the same.

The cost of operating has been very low. The volume of gas treated will average about 6,000 cubic feet (170 cub. m.) per minute. The power required is about 2.5 k.w., at a voltage of 35,000 to 40,000. As to labor, one man working one or two hours per day can keep the treater clean and in good running condition. Aside from the substitution of lead-covered frames for the cast-iron previously mentioned, very few repairs have been necessary.

It will be noted that the gases, having previously passed through a system of flues and a water scrubber, are comparatively cool and saturated with moisture. Attempts have been made, at times, to treat the dry gases coming from the flues directly, cutting out the scrubber. The results obtained under these conditions are much poorer than when the scrubber is in circuit. The temperature is, of course, much higher, being about 150° F. (66° C.) in the latter case to 300° F. (149° C.) in the former. The deposit is extremely dry and light, so that particles falling off the electrodes are carried out by the moving gases. The corona is not so good when dry gas is used, and if the voltage is raised there is much more sparking-over than when wet gas is passing.

In our case the presence of suspended moisture appears to be a very desirable condition to satisfactory precipitation of the fume. The injection of steam has been tried but did not give satisfactory results.

Recently, a system of sprays has been placed transversely in the lead flue leading to the treater inlet through which the gases are forced to pass, and with this arrangement we have secured better results than with any other, a number of tests having given silver escaping as low as two or three ounces (55 to 85 grams) per day. This, however, is while operating at less than the full furnace capacity.

The results obtained with the first installation have, on the whole, been so satisfactory that it was recently decided to build a second treater of sufficient capacity to give us practically complete precipitation of fume with additional furnaces operating.

For a number of reasons, among them being better insulation, more substantial construction, greater economy of space and ease of cleaning, it was decided to build the new treater of the tube type. From results obtained in numerous tests on pipes of varying dimensions, lead pipes, 18 inches (45 cm.) in diameter by 12 feet (3.6 m.) long, containing a single central discharge electrode, were found to be the most satisfactory.

The discharge electrodes, to be used in these pipes, are made of $\frac{7}{8}$-inch (2.2 cm.) steel shafting covered by extrusion with a star-shaped layer of lead. These electrodes are supported firmly over the pipes, and as they are stiff they require no steadying inside the treater. This is a very desirable feature. Most of the discharge at the start takes place from the sharp ridges extending the length of the electrode. However, when they have become coated with a deposit of dust the discharge is very uniform over the whole surface. With these pipes and a voltage of from 85,000 to 90,000 it has been possible to get over 99 per cent precipitation efficiency, at a gas velocity of 4.5 feet (1.35 m.) per second.

The electrical apparatus secured for the new treater consists of two 10-k.w., Fort Wayne, direct-connected, rotary converters, so arranged that they can be used interchangeably as a motor-generator set, or, as rotary converters. As a rule, they will be operated as a motor-generator, in which case the generator is separately excited by the regular 220-volt lighting current. Alternating current at 25 cycles and up to 200 volts can be obtained from these machines.

The transformer was made by the American Transformer Co., and is of 10 K. V. A. capacity. It is oil-cooled and has five taps giving 50,000-62,500-75,000-87,500-100,000 volts at a primary voltage of 200. By means of these taps, together with rheostats in the generator field and in series with the low tension A. C., it is possible to secure extremely fine regulation of the high-tension voltage.

An arm-type rectifier of Research Corporation design is used, and has proved very satisfactory in all the tests which have been made.

With this complete installation we expect to be able to treat up to 12,000 cubic feet (340 cub. m.) per minute of silver furnace gases and to recover 99 per cent of all the silver and gold which they contain.

According to the "Kavkaz" a group of Russian leather manufacturers are establishing in the West Caucasus a large plant for the production of oak and chestnut bark extract. It is stated that the capital, $7,500,000, has been fully subscribed. Heretofore Russian manufacturers have been dependent on the imports of tanning extracts from the United States.

The coal production of France in 1914 amounted to 29,786,505 metric tons, compared with 40,843,618 tons in 1913.

STELLITE.*

By ELWOOD HAYNES.

The name "Stellite" was coined from the Latin word "Stella" a star. This name was first applied to a binary alloy consisting of Cobalt and Chromium, which the writer discovered and produced as early as 1899. It was not until some years later that its properties were fully investigated, when it was found to possess the following properties:

1. A considerable amount of hardness, as alloys containing 10 per cent or more of chromium could not be successfully filed, though the file could slowly wear away the surface of the metal.

2. Considerable toughness. Alloys containing as high as 25 per cent chromium showing elongation of 10 per cent or more.

3. Comparatively high tensile strength and elastic limit. A bar of forged metal showing elastic limit of 85,000 lbs. and tensile strength of 110,000 lbs.

4. Fine color and lustre. The color of the alloy lies between that of steel and silver.

5. Absolute resistance to oxidation or other changes when exposed to either dry or moist atmosphere at all temperatures under a dull red heat.

In 1911 the writer succeeded in producing very hard alloys (consisting essentially of cobalt and chromium) by adding tungsten or molybdenum or both. The hard alloys thus formed could not be scratched with the file, but in turn would scratch any steel that could be produced. Some of these alloys were extremely brittle and those used for lathe tools require very careful handling. Some of them that showed excellent cutting qualities when used for turning cast iron or steel would break very easily if subjected to any abnormal stress.

In order to determine the stress required to break a ⅜ in. sq. tool, for example, a small clamp was made in the form of a slot precisely similar to the slot used in the tool holder.

A short piece or bar of stellite was placed in this slot and pressure applied vertically near the end of the bar at a distance of 1 in. from the clamp. Some of the weaker bars broke at from 100 to 300 lbs. pressure under this test. Gradually the strength of the bars was increased until they would readily withstand 1,000 lbs., and at this time bars are produced for turning steel which readily withstand from 1,200 to 1,500 lbs. under the same test. The very hard bars used for turning cast iron usually stand from 800 to 1,200 lbs. under this test. Bars that would stand as high as 1,850 lbs. have been produced, but were not found to be equal in cutting qualities to some other compositions of slightly less strength. It should be remarked at this point that the cutting qualities of any steel do not depend primarily upon its strength, but upon the suitable combination of strength, hardness, resistance to wear, etc. The strength of a tool is in reality a question of elastic limit. Steels possessing this quality to the highest degree are nickel steels, nickel chrome steels and vanadium chrome steels. For turning steel and iron, however, they are of little or no value, since they lack in hardness and resistance to abrasion, particularly at high temperature.

The virtue of the stellite tool lies in its ability to maintain its cutting edge at a high rate of speed at temperatures which would immediately cause the failure of any known tools containing any notable quantity of iron. Its great *hardness* and resistance to *abrasion* at all working temperatures are likewise valuable properties.

Owing to the fact that stellite retains its hardness even at a full red heat it cannot be forged. This fact, however, is rather a virtue than a detriment so far as use is concerned, because if the alloy would soften sufficiently for forging when heated it would, of course, immediately lose its cutting edge at the same temperature and this would limit its usefulness to a marked degree.

From the above fact stellite can only be reduced to the desired form by casting it in dies in the form of bars which are afterward ground to a cutting edge. Its capabilities as a lathe tool are now universally acknowledged, though in certain cases failures have resulted, due to improper knowledge of the alloy and its peculiarities. It should be remembered that it is *not a steel* and therefore requires special handling, which enables the operator to utilize its valuable properties to the best advantage.

Without going into the method of handling the alloy, some results obtained by its use would, perhaps, not be out of place. It was recently ascertained that a ⅜ in. sq. by 2½ in. long piece of stellite, ground to the form of a grooving tool, cut 14,000 grooves in cast iron pistons ranging from 3½ in. to 4⅜ in. in diameter before it became too much worn off for further use. This work was performed in regular practice and not as a test. A still more remarkable and more recent performance has just come to light in the same factory. A stellite tool of the same dimensions as that mentioned above, but which was ground to the round nose form and used for turning pistons, turned off more than 8,000 lbs. of cast iron before becoming too short for use. Considering only the portion of the tool which was actually ground away, the tool turned off 1,000 times its weight of cast iron before becoming too short for service.

Both of the above tools were made especially for turning cast iron. Another combination is used for turning steel, which has also shown equally remarkable results. These tools are now being used extensively for turning shrapnel shells at high speed for the European war.

While long wear is an important property in a lathe tool, it is not the essential or most valuable property. The value of the tool, even at the comparatively high price of stellite sinks into insignificance when compared with the value of the *time* saved. For example, in the cast iron performance mentioned above, the stellite cost only about 1c per day, while it effected a net saving of from $2.00 to $3.00 per day. In other words, it is the value of the *output* which counts and not the cost of the tool.

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*Paper presented at the annual meeting of the American Institute of Metals, Sept. 28 to Oct. 1, 1915, at Atlantic City, N. J.

HEAT LOSSES FROM AN ELECTRIC STEEL FURNACE.*

By W. H. WILLS and A. H. SCHUYLER.

The furnace investigated is at the plant of the Treadwell Engineering Co., Easton, Pa., and has been already described in these Transactions (1914, of the American Electrochemical Society, 25, p. 133), where a full description of the furnace with its dimensions may be found. The furnace is of two-ton rated capacity, with magnesite brick hearth overlaid with burnt dolomite. The pouring spout is in the center of the front side and at each side is a charging door. Three cylindrical graphite electrodes 8 inches (20 cm.) in diameter pass through the roof, threaded for continuous feeding, and are used in 180-pound (82 kg.) sections three feet (90 cm.) long. The power supply is 40 kw., 3 phase, 60 cycle, alternating current, the potential between the electrodes being 80 volts and the normal current per phase 2,500 to 3,000 amperes. The Easton Light and Power Company furnishes the current, at 11,000 volts on the primary.

The object of the experiments was:

1. To investigate the heat losses due to gases issuing from charging doors and tap holes.
2. To investigate the heat losses by conduction into the electrodes and by the water jackets surrounding the electrodes.

Average Operating Conditions.

The product is high grade steel castings, carbon 0.05 to 1.20. Raw material, boiler punchings and structural steel scrap. Lime and some hematite are charged as flux, with fluorspar later. Coke dust is added toward the end of the run, to deoxidize the slag. Final additions of ferro-manganese, ferro-silicon, and aluminum are made. The average length of the heat is 4½ hours. Electrode consumption per heat (2 tons) about 60 pounds (27 kg.); per ton of steel 30 pounds (13.6 kg.); per kw. hour 0.0375 pound (17 grams). The average power input during the test was 350 kw.

I. HEAT LOSSES THROUGH ESCAPING GASES.

Sheet iron flues to facilitate collection of the issuing gases and their measurement were fitted to the furnace doors and tap-hole. The one for the charging doors had a 6-inch pipe, and the one for the tap-hole a 3-inch pipe. The temperature of the escaping gases was measured as they issued by a LeChatelier thermocouple, protected by asbestos tubing. The temperature of the gases leaving the pipes, where the velocity was measured, was taken by suitable mercury thermometers. The velocity of the gases issuing from the 3-inch pipe was measured with 2½-inch (6 cm.) anemometer and on the 6-inch (7.5 cm.) pipes and with a 6-inch anemometer. An Orsat apparatus was used to analyze the escaping gases.

On the first test, run April 16, 1915, the length of the run was four hours twenty-five minutes. The sheet iron flues were placed over the charging door openings and tap hole, and carefully plastered around with fire clay. The following observations were taken at approximately equal intervals:

1. Temperature of gases escaping through the door and tap hole.
2. Temperature of gases leaving pipes.
3. Velocity of gases leaving pipes.
4. Power input to the furnace.
5. Sample and analysis of furnace gases.
6. Barometer reading.

In taking the temperature of the escaping gases, the hot junction of the thermocouple was placed at different points in the openings, and an average reading of the temperatures of gases escaping was obtained.

The following table gives a general log of the observations taken:

TABLE I.

Time	Initial Temperature of Gases, C°.	Temperature of Gases leaving Pipes, C°.	Velocity of Gases leaving Pipes Feet per Minute.	 Meters per Minute.	Power Input, Kw.
12:30	Furnace charged.				
1:30	door 1.....745	215	310	80	300
	door 2.....755	158	340	86	
	tap hole....716	202	300	76	
2:00	door 1.....755	230	295	75	390
	door 2.....723	142	290	73	
	tap hole....735	312	240	61	
2:30	door 1.....774	242	335	85	390
	door 2.....784	117	290	73	
	tap hole....735	256	260	66	
3:00	door 1.....842	255	320	81	350
	door 2.....832	110	256	65	
	tap hole....745	230	300	76	
3:15	door 1.....866	265	334	85	360
	door 2.....804	108	260	66	
	tap hole....876	192	288	73	
3:30	door 1.....903	270	325	82	350
	door 2.....850	110	245	62	
	tap hole....920	235	292	74	
4:00	door 1....1000	282	350	89	350
	door 2.....929	115	250	64	
	tap hole....973	195	300	76	
4:30	door 1....1018	210	370	94	370
	door 2.....964	112	255	65	
	tap hole...1010	203	284	72	
5:00	Furnace tapped.				

TABLE II.—ANALYSES OF GASES.

Time.	Opening.	CO_2	O_2	N_2
1:30	door 2	3.6	18.6	79.2
2:00	tap hole	1.8	9.4	78.8
2:30	door 2	0.4	20.2	79.4
2:50	tap hole	5.0	16.9	78.1
3:15	tap hole	3.0	18.1	78.9
4:00	door 1	3.2	14.9	81.9

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*Paper presented at the 28th general meeting of the American Electrochemical Society, in San Francisco, Sept. 16-18, 1915.

II. ELECTRODE HEAT LOSSES.

The furnace was provided with three electrodes passing through the roof of the furnace, each being in sections of about three feet long and weighing 180 pounds per section (82 kg.). In the electrode holders electrical connection is made by copper plates screwed fast against the graphite and connected to the bus bars by heavy stranded copper cables.

The tests on electrode heat losses were run on April 17, 1915, from 9:35 a. m. to 1:35 p. m. Two chalk marks were made on each electrode between the water jacket and the electrode holder. The temperature of the incoming and outgoing water for the electrode water jackets was measured with ordinary thermometers.

The following observations were taken every half hour:

1. Temperature on the electrode surface at each chalk mark.
2. Power input to the furnace.
3. Current passing through each electrode.
4. Temperature of cooling water entering and leaving water jackets.
5. Rate of discharge of cooling water.

The temperature of the electrode surface was taken by a thermocouple pressed by a small piece of asbestos tightly against the surface of the electrode. From these observations the calories carried away from the electrode by the cooling water and by conduction through the electrodes could be calculated, using the heat conductivity of graphite for the range of temperature observed.

Table IV contains the record of water entering and leaving the cooling jackets and its quantity.

Table V shows the reduced values of heat losses in cooling water per minute at each of the 8 observations.

In Table VI t_1 is the temperature at the upper chalk mark, t_2 the temperature at the lower chalk mark, and the next column gives the difference in temperature in centigrade degrees, for each of the three electrodes, at the times given.

Table VII was calculated using the following data:

Cross section of each electrode 50.265 square inches (324 sq. cm.). Length of electrode between observation points, as follows:

	Electrode No. 1.	Electrode No. 2.	Electrode No. 3.
9:45 A. M. observations...	8 inches (20 cm.)	7 inches (17.5 cm.)	7.5 inches (18.5 cm.)
Other observations	4.87 inches (12.2 cm.)	4.87 inches (12.2 cm.)	5.25 inches (13.1 cm.)

Electrical resistivity of the graphite assumed 0.0003325 ohms per inch cube.

Thermal conductivity of graphite assumed 3.71 watts per inch cube.

These values were assumed as average values for the range of temperature concerned.

From these data calculations of the flow of heat in kilowatts were made according to the methods of Carl

TABLE III.—HEAT LOSSES.

Time.	Opening.	Corrected Vol. Escaping Gases per Minute, Cubic Meters.	Temp. C°.	Calories Lost per Minute.	Kw. Lost.	Total Loss, Kw.
1:30	door 1....	1.1	745	273.5	19.07	44.4
	door 2.......	1.216	755	304.8	21.25	
	tap hole.....	0.247	716	58.4	4.08	
2:00	door 1.......	0.932	755	245.3	17.10	40.00
	door 2.......	1.093	723	274.0	19.12	
	tap hole.....	0.202	735	54.1	3.78	
2:30	door 1.......	1.006	774	256.7	17.9	41.8
	door 2.......	1.162	784	796.1	20.65	
	tap hole.....	0.194	735	46.4	3.24	
3:00	door 1.......	0.941	842	267.5	18.62	39.00
	door 2.......	0.832	832	233.	16.27	
	tap hole......	0.233	745	58.1	4.06	
3:15	door 1.......	0.961	866	277.8	19.38	44.40
	door 2.......	0.073	804	288.1	20.10	
	tap hole......	0.242	876	70.7	4.93	
3:30	door 1.......	0.930	903	288.9	19.64	44.40
	door 2.......	1.010	850	285.3	19.92	
	tap hole......	0.225	920	69.4	4.84	
4:00	door 1.......	0.975	1000	329.9	23.00	50.85
	door 2..	1.014	929	316.7	22.10	
	tap hole......	0.251	973	82.4	5.75	
4:30	door 1.......	1.180	1018	406.9	28.37	57.50
	door 2.......	1.038	964	337.7	23.55	
	tap hole......	0.234	1010	80.00	5.57	

TABLE IV.—LOG OF COOLING WATER.

	Cooling Water			
	Entering	Leaving	Quantity per Minute	
Time.	C°.	C°.	Lb.	Kg.
9:45 A. M	8.5	17.5	42	19.05
10:40 A. M..............	8.5	15.5	42	19.05
11:05 A. M..............	8.5	16.0	42	19.05
11:30 A. M..............	8.5	19.0	42	19.05
12:00 M.	8.5	20.5	40	18.15
12:30 P. M..............	8.5	23.0	40	18.15
1:00 P. M..............	8.5	25.5	42	19.05
1:30 P. M..............	8.5	26.0	42	19.05

Furnace charged at 9:35 A. M.
Furnace poured at 1:35 P. M.

TABLE V.—HEAT LOSS IN WATER JACKETS.

Time.	Calories per Minute.	Kw.	Power Input.	Percentage Energy Loss
9:45	171.45	11.95	200	5.97
10:40	133.35	9.3	360	2.58
11:05	14.28	9.97	375	2.66
11:30	200.	13.95	350	3.99
12:00	217.8	15.18	400	3.80
12:30	263.4	18.38	300	6.13
1:00	324.	22.6	300	7.53
1:30	334.	23.3	310	7.50
				Average 5.20

TABLE VI.—TEMPERATURE OBSERVATIONS ON ELECTRODES.

	Electrode No. 1.			Electrode No. 2.			Electrode No. 3.		
Time.	t_1	t_2	t_2-t_1	t_1	t_2	t_2-t_1	t_1	t_2	t_2-t_1
9:45 A. M....	208	293	85	230	304	74	230	304	74
10:40 A. M....	227	293	66	230	293	63	241	329	88
11:05 A. M....	241	316	75	241	293	52	251	329	78
11:30 A. M....	251	328	77	230	293	63	241	328	87
12:00 M........	251	328	77	241	305	64	251	334	83
12:30 P. M....	230	294	64	241	305	64	209	316	107
1:00 P. M....	241	305	64	251	328	77	262	360	98
1:30 P. M ...	230	305	75	209	294	85	230	328	98

TABLE VII.

Time.	Electrode No. 1, Kw.	Electrode No. 2, Kw	Electrode No. 3, Kw.	Total Kw.	Power Input Kw.	Percentage of Power Input
9:45........	1.221	1.918	1.783	5.622	200	2.81
10:40........	2.412	2.281	3.011	7.704	360	2.14
11:05........	2.775	1.894	2.612	7.261	375	1.93
11:30........	2.855	2.229	2.874	8.019	350	2.32
12:00........	2.805	3.237	2.813	7.945	400	1.99
12:30........	2.344	2.677	3.370	8.441	300	2.81
1:00........	3.367	2.876	3.403	8.646	300	2.88
1:30........	2.784	3.171	3.403	9.358	310	3.02
					Average	2.10

Hering, Transactions of the American Institute of Electrical Engineers (1910) 29, 285, with the following results:

The following table gives the rate of total electrode loss by cooling water and by conduction through the electrodes and its percentage of the power input of the furnace:

TABLE VIII.

	Cooling Water, Kw.	Electrodes, Kw.	Total Kw.	Power Input, Kw.	Percentage Loss
I.........	11.95	5.622	17.572	200	8.79
II.........	9.30	7.704	17.004	360	4.75
III.........	9.97	7.261	17.231	375	4.60
IV.........	13.95	8.019	21.969	350	6.26
V.........	15.18	7.945	13.125	400	5.78
VI.........	18.38	8.441	26.821	300	8.94
VII.........	22.60	8.646	31.246	300	10.42
VIII.........	23.30	9.358	32.658	310	10.53
					Average 7.30

GENERAL REMARKS.

Both tests were run when the furnace was in good operating condition, for a new lining had been put in the day previous to the first test.

The door heat-loss measurement was by far the most difficult, owing to the necessity of handling the hot flues and fitting them tightly over the door openings. Several factors combine to vary the amounts of gas escaping through the different doors. Chief among these is the direction of the air currents through the foundry. Thus, during the latter part of the run a noticeable draft was blowing toward the right-hand charging door (No. 2) so the volume of gas escaping through this door was reduced while a corresponding increase was produced in the volume escaping from the tap hole (No. 3) and especially in the volume escaping from the left-hand charging door (No. 1). These changes are clearly shown by the gas volumes issuing from the different doors.

Each time flux was added to the bath the gas volume was appreciably increased for several minutes while flames shot out through the door openings. Just after the furnace is charged the gas volume is greater, due to the driving off of moisture and other volatile constituents of the charge and to the combustion of oil on the scrap steel. This probably accounts for the high heat loss through the doors at the beginning of the run.

As shown by the tables the loss increased toward the end of the run, being a maximum at tapping time. This is perfectly natural, for it is at that time that the furnace temperature is a maximum.

There is comparatively little gas generated in the simple melting-down operation. It was observed that a considerable portion of the furnace gases must be supplied by cold air flowing in under the charging doors through the opening between door and sill, where an appreciable in-draft was noticed. The furnace thus has to heat up this unnecessary air and then discharge it at a high temperature through the openings at the top of the charging doors and tap hole. This means lower efficiency.

The charging-door loss could be reduced very materially by making the doors fit closely against the furnace walls so as to cut off as much as possible the air flowing in at the bottom and the outgoing gases through the opening at the top. In the design of subsequent furnaces of this type two methods could be employed to accomplish this result:

First. By the use of a round charging door in the form of a plug mounted to swing on vertical trunnions. This does away with counter weights and permits the door being made thick enough to reduce leakage to a small amount.

Second. By having the furnace walls slightly inclined inward at the charging door ends and using vertically sliding doors with counter balance. The pull of gravity would then hold the doors with sufficient firmness against the walls.

The electrode heat loss is a necessary evil. Of course, the more electrodes through the roof the greater this loss amounts to, so the only way to minimize this loss on a small furnace is to run on single phase. Graphite electrodes were used on this furnace, which means a higher heat loss than with amorphous carbon electrodes.

The high electrode loss at the beginning was due to the fact that the electrodes, which were very hot from the previous heat, had been raised up to allow for the new charge, so that the surface ordinarily well below the water jackets was exposed and the portion next to the water jackets was red hot. This made the surface temperatures at first higher than they would be if the furnace was started cold. As the furnace temperature rose toward the end, the electrode loss naturally rose. This rise was more noticeable in the heat carried off by the cooling water than in that traveling up the electrode by conduction. The temperature at the two marks on each electrode did not change as much as might be expected, because the electrodes, after being pushed a maximum distance down into the bath when the charge was first melted down, were gradually withdrawn, so that the marks rose higher and higher above the water jackets. If the furnace temperature had remained constant, the surface temperature at the marks would have fallen.

The formulas used in calculating the heat passing out through the electrodes depend on the assumption that the electrodes have uniform cross section throughout their length, that the conductivities for heat and electricity are linear functions of the temperature, and neglect the loss by radiation from the electrode surface between the points at which the temperatures were taken. Since the distance between these points was comparatively small this radiation loss amounted to very little. The electrodes were uniform in cross section throughout.

The heat carried off in the water from the electrode water-jackets is not all from the electrodes, but a considerable part is from that part of the roof adjacent to the electrode openings. However this loss is made necessary by the electrodes and so may be counted under the head of electrode losses.

CONCLUSION.

By integrating the door and electrode loss curves and dividing these areas by their length, the average door and tap hole loss was found to be 12.5 per cent and the electrode loss 7.3 per cent of the power input to the furnace. The electrode loss can not be cut down much so long as graphite electrodes are used, but the door loss can be reduced a considerable amount by making the charging doors fit closely against the furnace walls, and the tap hole loss reduced by suitable closing devices.

RUBBER SHIPMENTS FROM AMAZON VALLEY.

In July, 1915, the first month of the new crop year, according to Consul George H. Pickerell, Para, Brazil, exports of crude rubber from the Brazilian ports of Para, Manaos, and Itacoatiara to Europe were considerably less than half those for July, 1914; to the United States they were 30 per cent larger, this increase being distributed among the four grades of rubber that constitute the shipments from the Amazon valley as Table I shows:

TABLE I.

Exported from—	Fine. Pounds.	Medium. Pounds.	Coarse. Pounds.	Caucho. Pounds.	Total. Pounds.
Para to—					
United States	735,336	200,989	837,909	842,318	2,616,552
Europe	328,035	17,361	22,020	452	367,868
Manaos to—					
United States	335,806	47,476	147,337	299,778	830,397
Europe	317,768	47,571	8,025	44,055	417,419
Itacoatira to—					
United States	......	......	......	......	......
Europe	13,389	331	6,329	1,517	21,566
Total, July, 1915, to—					
United States	1,071,142	248,465	985,246	1,142,096	3,446,949
Europe	659,192	65,263	36,374	46,024	806,853
Total, July, 1914, to—					
United States	750,826	145,357	808,382	947,639	2,652,204
Europe	713,974	93,037	133,267	1,041,536	1,981,814
Grand total, July, 1915	1,730,334	313,728	1,021,620	1,188,120	4,253,802
Grand total, July, 1914	1,464,800	238,394	941,649	1,989,175	4,634,018

The outlook for an abundant supply of oil in the Flathead Valley, just over the Montana state line in the extreme southeastern corner of the Fernie consular district, is said to be bright. While the company that is working the field does not claim to have struck pay oil as yet, it is announced that oil sands have been struck at 800 ft. Drilling was begun July 20 and the first signs of oil were encountered Sept. 20. Two standard drilling plants are in operation.

According to the Hull correspondent of the Oil and Color Trades Journal, the imports of linseed oil at Hull, England, during the first seven months of 1915 amounted to 51 per cent of the United Kingdom total.

UNFAIR FOREIGN COMPETITION.

Many inquiries have been received by the Bureau of Foreign and Domestic Commerce as to the prevention of unfair foreign competition against the new American industries established during the war. In view of this the Secretary of Commerce has addressed the following letter to the chief of this Bureau:

> If the question arises as to the attitude of the Department of Commerce toward what is called "dumping" after the war shall end, you may say that I shall recommend in my annual report that unfair competition from abroad shall not be permitted to injure a legitimate American industry any more than it is permitted to do so in our domestic field. Especially I shall oppose action on the part of any foreign monopoly toward controlling the American market by unfair competition in an attempt to injure or destroy an American industry. There is no doubt in my mind that this should be done. The more serious question to which consideration is being given is as to the method of doing it. Various plans have been proposed, some of which seem to permit reactions which are possibly undesirable. I am considering the methods used in different countries, with a frank preference for such as have nothing to do with tariffs or duties. I should be very glad to receive suggestions from practical commercial men as to the most efficient means of detecting and preventing this unfair competition.
>
> You may be quite sure of my earnest purpose to provide, so far as it lies in my power to do so, that American industries shall not suffer from a type of unfair competition at the hands of foreign producers which would be forbidden if it took place at the hands of American producers.
>
> There is no reason why you should not make known this expression of my views.
>
> William C. Redfield.

The receipt of the final forecast of the Indian jute crop, according to the Glasgow Herald of Sept. 22, had no effect on the Dundee (Scotland) market one way or the other. The final estimate places the current season's acreage in India at 2,377,000, against 3,358,737 acres last year; and the yield at 7,428,733 bales (of 400 pounds), against 10,531,505 bales. The yield is 3.13 bales per acre, which is in keeping with the result last season, showing that the shortage in India's production this year is due to reduction in the area cultivated.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

A Study of the Quality of Platinum Ware.

At the suggestion of a committee of the American Chemical Society, the Bureau of Standards of the Department of Commerce has made an experimental study of the quality and purity of platinum utensils, such as crucibles, wire gauze, dishes, etc., and has developed a delicate thermoelectric test for platinum purity which permits a rapid estimate to be made of the amount of included foreign matter, such as iridium or iron, without injuring the article tested. This thermoelectric test is being generally adopted by large purchasers of platinum ware. The losses in weight on heating and after acid washing have been determined for several grades of platinum crucible, including pure platinum, and ware containing iridium or rhodium, and also iron. From the results of this investigation it is now possible to predict very closely what will be the loss in weight of a "platinum" crucible when heated, thus eliminating a serious source of uncertainty in exact analytical chemistry. Ordinary grades of platinum are found to lose from 0.7 to 2.7 milligrams per hour per 100 square centimeters of surface at 1,200° C. Curiously enough the small amounts of iron always present in platinum are found to bear no simple relation to the magnetic properties. Suggestions are also given concerning specifications for the purchase of platinum crucibles.

Testing and Properties of Textile Materials.

The Bureau of Standards, Department of Commerce, has recently revised and enlarged its Circular No. 41, relating to the testing and properties of textile materials. Several changes in wording have been made to eliminate misunderstandings that have occasionally occurred. Other changes have been necessitated by the adoption of new and improved methods of testing, all of which are explained in some detail. Several photographs and diagrams have been added to assist in describing some of the apparatus used. The new circular contains a general consideration of the procedure used in testing textile samples submitted in connection with purchases by the various departments of the Government. These samples include raw fibers, rope, twine, thread, yarn, and all forms and kinds of fabric. A very large amount of such materials is purchased annually by the Government, and it is therefore necessary to use great care that the proper value is obtained. Besides the work done for the Government, the Bureau of Standards also does testing for private persons in cases of dispute or when proper facilities are not available elsewhere. For the information of those interested a schedule of fees has been appended, thus enabling those who will need to have tests made by the bureau to estimate the probable cost. Very often work is done free of charge when the bureau considers it to be of such a nature that it will give information valuable to the bureau in solving some of its many scientific and practical problems.

Silesian Coke Production and Market.

U. S. Consul Harry G. Seltzer, at Breslau, Germany, reports that according to an official announcement, the Silesian coke production in May, 1915, reached the high-water mark of 1,788,000 metric tons, an increase of 9 per cent over the preceding month and of 3 per cent over May, 1914. About 161,000 tons were exported in May, against 141,000 tons in April. In normal times the average monthly export is about 450,000 tons. Although manufacturers always had some difficulty in marketing their output in peace times, the demand is now just about equal to the supply. This is due, first, to the reduced quantities of coal mined since the opening of the war on account of the lack of labor; and second, to the larger use of coke by railroads and manufacturing plants as a substitute or as a supplement to coal. The demand is further steadied by the large contracts with the railways and with the factories, foundries, and electrical works which are now engaged in furnishing army supplies. Individual consumers have to be satisfied with such quantities as may remain after these large Government contracts have been filled. Of the smaller sorts (crushed coke) larger quantities are again offered for sale, since most of the coke manufacturers have enlarged their plants for the production of by-products. However, it may be said in general that sales are still limited as to quantity and date of delivery. The future of the coke industry will depend largely upon the labor supply and the consequent increase of coal production to its normal basis. Coke manufacturers are rather cautious about the extension of their plants and are not attempting to do any more than meet immediate demands. On account of the decreased supply of steam coal, the demand for coke is steadily increasing. Whether this demand will continue to grow will be largely determined, first, by the supply of coal available; second, by the results of mixed (coal and coke) firing; and, third, by the price at which coke may be produced under improved conditions and a steadier market. Following the example of the Prussian Government Railways, which consume about 240,000 tons of coke monthly, other railway administrations are also beginning to use coke in large quantities in connection with coal. In addition to these demands dealers and consumers are anxiously looking for their autumn supplies, with the result that prices are steadily advancing.

New Method of Making Sulphuric Acid.

A new method of manufacturing sulphuric acid, for which advantages are claimed, is suggested in United States Department of Agriculture Bulletin No. 283, "The Production of Sulphuric Acid and a Proposed New Method of Manufacture." The essential difference of the method is that the gases employed are drawn downward through a spiral flue in place of being drawn through lead chambers or intermediate towers. It is asserted that the resistance of gases to the downward pull and the constant change in their course through the spiral tend to mix them very intimately. The fact that the gases constantly impinge on the walls of the spiral flue, which can be cooled either by air or water, makes it practicable to maintain the gases at a temperature most favorable for the efficient yield of sulphuric acid. In laboratory tests in which the spiral was utilized practically all the sulphur dioxid was oxidized to sulphuric acid, only traces being lost through escape or in the system. The lead spiral, the author points out, however, is not intended to replace the Glover tower, nor to do away with the Gay-Lussac tower. It is believed that while the lead spiral will take considerable lead, the great reduction it will effect in the chamber space will make it possible to construct a plant with considerably less lead than is required in the ordinary chamber system. The new type of plant requires no other device to accelerate the reactions, occupies much less ground space, and would not need as large buildings, and therefore should decrease the initial cost of construction. The method, however, has been tried only on a laboratory scale, and the bulletin refuses to predict just how efficient the commercial plant would be, but states that all indications are that this method offers promise of being economically successful.

Inflammability of Mixtures of Gasoline Vapor and Air.

The inflammability of mixtures of gasoline vapor and air is discussed by G. A. Burrell and H. T. Boyd in Technical Paper 115, just issued by the United States Bureau of Mines.

The authors in their conclusions say in part: "Two methods for determining the content of gasoline vapor in air are discussed. One has to do with the introduction of the mixture into an exhausted glass vessel, cooling it at the temperature of liquid air, removal of the air, and finally the measurement of the partial pressure of the gasoline vapor by means of a manometer attached to the liquefaction bulb.

"Another method consists in burning the gasoline vapor in oxygen and, from the contraction and carbon dioxide produced, calculating the percentage of gasoline vapor.

"When a 100-c.c. Hempel explosion pipette was used and the mixtures were ignited from the top, there was obtained as the lower limit of complete inflammation a value lying between 1.9 and 2.0 per cent of gasoline vapor. The upper limit under these conditions was found to be between 5.2 and 5.3 per cent of gasoline vapor. The gasoline used had a specific gravity of 73° B. Under the same conditions, except that the mixtures were ignited from the bottom, there was obtained a value lying between 1.5 and 1.6 per cent of gasoline vapor as the low limit. With the same grade of gasoline, with a 2,800-c.c. vessel, and with ignition from the bottom by means of an electric flash produced by pulling apart two wires through which a current of 7 amperes at 220 volts was flowing, there was obtained a value lying between 1.4 and 1.5 per cent of gasoline vapor. The high limit under these conditions lay between 6.0 and 6.4 per cent of gasoline vapor.

"When the initial temperature is increased before ignition of the mixtures the low limit is gradually decreased until with an initial temperature of 400° C. the low limit lies between 1.02 and 1.22 per cent of gasoline vapor.

"The range of complete combustion for mixtures of gasoline vapor and air is very narrow, and is between about 1.5 and 2.5 per cent. The amount of carbon dioxide produced reaches a maximum at 2.5 per cent of gasoline vapor. At this point, as the percentage of gasoline vapor increases, carbon monoxide begins to form. At 4.1 per cent of gasoline vapor there is produced 14.0 per cent of carbon monoxide."

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SOME AMERICAN CONTRIBUTIONS TO INDUSTRIAL CHEMISTRY.*

By SAMUEL P. SADTLER, PH.D.

You will notice that I have limited the subject matter of my brief address to what I call American Contributions to the Field of Industrial Chemistry. And even this field I will restrict by leaving to one side, the discussion of what we have contributed to well-established industries of European origin, or how we have worked on lines already clearly mapped out for us by the prior establishment and successful operation of those industries abroad.

I do not wish to say that such contributions of American Chemists to some of the older and long-established industries have been of so slight a value as to be unworthy of mention. On the contrary, the part that American chemists and engineers have taken in the development of some of the older industries, such as the manufacture of acids, alkalies, and of heavy chemicals, of pigments of soaps and glycerin, papermaking, leather manufacture, and certain metallurgical lines, has been quite important. Most of this has received deserved recognition in the series of reports prepared within the last year for the Industrial Division of the American Chemical Society and published in its *Journal of Industrial and Engineering Chemistry*.

However, there are some very important chemical industries that took their start with us in this country and have been developed, too, in most cases, to flourishing condition without borrowing any notable help from abroad. These we should point out to those of the public who have not learned that we have anything distinctively our own as yet, and who think that because we cannot command our ante-bellum supplies of potash and organic dye-colors at present we must start in and establish the manufacture of chemicals as a new venture for this country.

With the wonderful richness of this country in the raw materials which lie at the basis of chemical industries, and with the well-known inventive and mechanical turn of our people, we would be greatly disappointed if we did not find some results in the way of the establishment of new and distinctive lines of manufacture and the production of new products for which uses were speedily found. We desire to make, this evening, brief reference to some of these American-developed chemical industries.

The first to note chronologically as well as the first in importance is the great petroleum industry. Isolated occurrences of natural oils, combustible in character, had been observed in various parts of the world, just as natural gas had been noted as a matter of interest to the mineralogist and to the traveler. For instance, in 1833, the elder Silliman and, in 1836, Dr. S. P. Hildreth described the occurrence of oil springs. From the surface of these the Indians had collected what was called Seneca oil. I have myself a pint sample of such oil from a spring in Ohio that is reported locally to have yielded oil from 1813 to the present. The Rock Oil Company, which afterwards became the Seneca Oil Company, had engaged Col. E. L. Drake as its manager, and on August 28, 1859, he struck oil at a depth of 69 feet in a well that he had drilled near Titusville, Pa., which started off with a daily yield of 25 barrels. From this mustard-seed has grown the great American petroleum industry, which in 1914 produced 265,762,535 barrels or 66.36 per cent of the world's production.

However, it is not simply a question of being first in the discovery of how to obtain the oil from its subterranean deposits. The distillation of the crude oil for the purpose of separating the lighter from the heavier portions and refining them so that they could be used as burning oils, lubricating oils, etc., was developed entirely independently in this country. The distilling of shale oil and the preparation of a merchantable product for use as an illuminant under the name of "coal-oil" had already been practiced when Drake's discovery was announced and petroleum distilleries speedily sprang up. Then the accidental discovery, as it is claimed, of the possibilities of increasing the yield of light fractions by what is known as "cracking," about 1865, made it possible to get a maximum yield of kerosene fraction from the crude.

When, later, the large production of a crude oil in California, differing greatly from the Pennsylvania crude first developed industrially, led to the establishment of the distinction between paraffin-base crudes and asphalt-base crudes, the preparation of an artificial asphalt from California oil followed.

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*From an address at the National Exposition of Chemical Industries, New York, Sept. 24, 1915.

Because of the large utilization of asphaltic materials for paving, roofing, waterproofing, etc., the manufacture of artificial asphalts by the blowing of hot oil residuums generally, according to either the Byerley or the Culmer patents, followed, and it is now possible to get, in this way, solid products of every grade of ductility and penetration and a wide range of melting-point which find a great variety of uses.

It must not be overlooked that the industry owes much also to the engineering ability of the men connected with its early development. The enormous extent of the producing field would have made the question of the transportation very serious had not the tank car and the pipe-line soon developed to relieve them. These were the fruit of American invention, while the Russian oil industry is to be credited with the introduction of the oil-tank steamer now in general use.

I have referred to the early use of "cracking," as practiced in the handling of the crude oil stills of most refineries in order to increase the burning oil fraction at the expense of the heavy oils. This has been followed by efforts to increase notably the gasoline or light naphtha percentage, which in recent years has become more important and commands a higher price than the burning oil. In place of the cracking by causing condensed heavy vapors to drop back upon a superheated oil layer in the still, but working under normal pressure, which involves much waste by formation of uncondensable gas and separation of carbon, recourse was had to distillation under pressure, as in the Burton process, now largely used by the Standard Oil Company in several of its largest refineries and with a considerable measure of success. Still more recently the principle of distillation under heavy pressure and at higher temperatures has been brilliantly applied by Dr. Rittman, with the result of the production of large amounts of gasoline or, at higher pressures, of benzene and toluene (aromatic hydrocarbons) in notable amount. This process is now being given a large-scale experimental trial by the Ætna Chemical Company, of Pittsburgh.

A somewhat similar process of decomposition of petroleum by heating under very high pressure has been described in outline by Walter O. Snelling, but the full account of the method and results has not as yet been published.

Radically different from these processes of cracking under pressure is the recently described process of McAfee, who utilizes the Friedel and Crafts reaction with anhydrous aluminum chloride and, after getting off the normally present gasoline and kerosene, runs the distillation of the heavy oils at about 500° to 550° F. with the aluminum chloride, obtaining, as a result, saturated hydrocarbons in both the gasoline and kerosene fractions produced. Mr. McAfee's paper has just recently appeared in both *Metallurgical and Chemical Engineering* and *Journal of Industrial and Engineering Chemistry*, and is worth careful study. I heard him give an account of his results at the San Francisco meeting of the American Institute of Chemical Engineers, and examined his samples of oils as used and obtained in his work.

My account of the American development of the petroleum industry would be incomplete did I not mention the rapid development of the production of gasoline by the condensation of natural gas accompanying crude petroleum, or what is called "casing-head gas." Bulletin No. 88 of the Bureau of Mines, Department of the Interior, on "The Condensation of Gasoline from Natural Gas," by Burrell, Seibert, and Oberfell, issued this year, gives a very complete picture of this new industry. I merely give the summaries of amounts of gasoline so produced in recent years: 1912, 12,081,179 gallons; 1913, 24,060,817 gallons. Of course, this gasoline with a gravity of 85° to 90° B. is reduced by blending it with naphtha distillate.

A second great industry developed in this country is the working up of native rock phosphate of lime into a fertilizer product. Of course, the value of phosphoric acid as an element in the fertilization of the soil was already indicated by Liebig, the great chemical founder of scientific agriculture, and the use of the rich native phosphates known as guano was extensively followed. But the opening up of the South Carolina phosphate rock beds in 1870, followed by the discovery of the still more abundant deposits of Florida in 1888 and of Tennessee in 1893, furnished the material for what was practically a new and American industry. The mining of rock phosphate and the manufacture of superphosphate fertilizers henceforth went hand in hand, with the result that one of the great chemical industries of America was developed. Reckoned by tonnage of products, it is the largest of our chemical industries, and it is important, too, as consuming fully one-half of the American sulphuric acid production, far exceeding all other industries in this respect.

I shall not take the time here to trace the development of this industry, but would like to add a few words to show the magnitude of our resources in raw materials in this line.

Dr. H. K. Benson, in his paper, read at the recent Seattle meeting of the American Chemical Society, on the "Resources of the Northwest," said that the phosphate deposits of Idaho were thirty times greater than the other deposits in the United States. The United States Geological Survey estimates that these Idaho deposits contain 2,500 million tons of phosphate rock with 35 to 37 per cent P_2O_5.

Related to this phosphate fertilizer industry is our utilization of animal scrap and waste for analogous use as fertilizer material. I will note three principal sources of supply of this material: First is the tankage and scrap of the great packing-houses at Chicago, Kansas City, Omaha, etc.; second, the menhaden fish residue of our Atlantic coast, after the oil has been extracted; and, third, the waste of the salmon and other fish-canning industries on the Pacific coast. With regard to this latter, Dr. H. K. Benson, in his paper on the "Resources of the Northwest," stated that from a packing of eight million cases of salmon in 1913, 140,210 tons of cannery waste was obtained. Of the amount of material from the other sources named I have no present information.

Another great industry, while not created *de novo,* has been profoundly modified by an American invention which was developed and in use here for years before it was taken up abroad. I refer to the water-gas manufacture. This was the invention of Thaddeus S. C. Lowe, who had already established a creditable reputation as a military aëronaut in our Civil War. The Lowe water-gas process of 1872-5 afterwards was acquired by the United Gas Improvement Company of Philadelphia and underlies the present large manufacture of this type of gas, whether carburetted or otherwise, which is practiced in this country and in Europe upon the continent. The Germans followed in 1886, and with an improved form of apparatus in 1895.

More recently we have seen another old-established chemical industry revoluntionized by an American invention, which had the effect of establishing what might be called a new and highly successful American industry. I refer to the American production of sulphur in Louisiana by the aid of the Frasch process of extraction of the sulphur in melted form by pumping it from the depths where it is found. This American production of a nearly pure native sulphur has completely stopped the importation of Sicilian sulphur, and was, at the outbreak of the present war, competing with the Sicilian product in Mediterranean ports.

We have two distinctively American products in the vegetable kingdom which serve to furnish the starting-point or raw materials for two highly-developed American chemical industries, viz., the cotton plant, furnishing the cotton seed and its products, and the maize or Indian corn, furnishing corn starch and its alteration products, corn oil and gluten.

The cotton seed and its products have become among the most valued assets of the cotton planter. From each ton of cotton seed over 300 pound (40 to 50 gallons) of oil can be obtained, which, when properly refined, furnishes us one of our most valuable oils, both for technical use, as soap stock, and for food purposes. Hundreds of mills throughout the south are engaged in pressing this cotton oil, as it is called; enormous quantities have gone to be blended with stearine to make so-called compound or substitute lard, and other large amounts brought to a white, deodorized condition, used directly for food and baking purposes. More recently it has been converted into a soft, white, solid condition by the hydrogenating treatment, and in that form is again available as an edible oil for cooking and baking. After the expulsion of the oil, we have left the oil-cake, which, ground to meal, makes a very valuable feeding stuff or addition to fertilizers because of its nitrogen content. The hulls, burned as fuel, yield an ash rich in potash and phosphoric acid, hence of immediate value in the making up of fertilizers. The success with which the cotton seed, at one time a waste product, after the removal of the seed hair or valuable fibre by ginning, has been turned into a source of wealth for a great section of our country, illustrates how a great chemical industry was built up and values created out of material at first entirely neglected. The other distinctively American industry that I coupled with the cotton seed industry was the utilization of maize or Indian corn, and has come to be known generally as the corn products industry.

While the starch production from wheat, potatoes, and rice had been worked out elsewhere, and while a hydrolyzed product of syrupy consistency had also been obtained from potato starch, the manufacture of corn starch and of corn syrup, the latter first known as glucose, was worked out in this country, and upon and around this has been built up a great industry, producing a great range of products of great commercial importance. Corn starch was manufactured in this country as early as 1848, at Oswego, N. Y., but until about 1881 little but the starch itself was recovered or sought to be recovered. Today, besides recovering the starch in a high state of purity, the germ is made to yield the valuable corn oil and an oil-cake for cattle feeding; the gluten is recovered in a dry state and, mixed with the ground hulls, makes a nitrogenous cattle food. The extractive matter (or corn-solubles) from the steep water is now also saved and incorporated with the gluten feed. The starch may be marketed as dry starch of various grades and prepared for a variety of uses, as dextrines of various colors and qualities, or as more or less hydrolyzed products, known as corn sugar and corn syrup. The oil is used in the manufacture of soap, soap powders, in the tanning industry and in paint, and, what is of interest, affords, when vulcanized, an excellent rubber auxiliary or rubber imitation. It is also a source of glycerin, while the free fatty acids find ready use by the soapmaker. In fact, this industry, in its present-day development, is one of the best illustrations of a scientific American chemical industry, working up a distinctive American raw material in the most complete way.

Without looking around for further individual illustrations of American-developed chemical industries, we now turn to a group of industries of American founding and developing which have taken a great lead in the world's industrial progress. I refer to the part which America has played in the electro-chemical and electro-metallurgical industries, several of the most important of which are based upon the discoveries of American chemists and have been brought to a high state of development by their continued effort.

The first of these American inventions was the Hall aluminum process, dating back to 1886, the date of his patent application. This fundamental discovery of the method of electrolyzing alumina dissolved in a bath of fused cryolite has now supplanted all other methods, and the manufacture of metallic aluminum everywhere throughout the world is practically based upon it. What is of more importance for our present argument is that a great American industry has developed from it and we have become the leaders in the manufacture of this important metal because of it. The history of this discovery has been repeatedly told and the importance of aluminum in the arts has been pointed out, so I will not dwell upon that side of the subject.

We have next two important industries, both based upon the discoveries of an American chemist. I refer to the carborundum industry and the manufacture of artificial graphite, both based upon the discoveries of Dr. E. G. Acheson and now flourishing lines of manufacture at Niagara Falls, N. Y. The carborundum or silicon carbide is formed in the electric furnace and finds an extensive use as an abrasive under a great variety of forms, having a hardness almost equal to that of the diamond. The artificial graphite is a product of a reaction similar to that indicated for carborundum, but carried through at a higher temperature, whereby the silicon is evaporated, leaving the residual pure carbon as soft metallic graphite. This latter is so free from impurity that it may serve as the basis of the finest lubricating mixtures. These specially-prepared lubricants, known as aquedag and oildag, according as they are brought in suspension in water or oil admixture, have proved of special value.

One of the great industries based upon electric furnace work is the manufacture of calcium carbide, which in itself, as a source of acetylene and as the necessary material for use in other great industries, as the cyanamide manufacture, is now produced throughout the world in large and increasing amount. While calcium carbide as a chemical compound had been discovered by Wöhler in 1862, and while Moissan had obtained it in his electric furnace independently about the same date as Wilson, the production of it by electric furnace reaction on a working scale was due to Wilson at Spray, N. C., in 1892, who may therefore be said to have founded the calcium carbide industry. This industry has spread to all countries where cheap water power is available for the generation of electricity, and in this country is strongly establish at Niagara Falls and at Sault Ste. Marie, besides the use above referred to in the manufacture of calcium cyanamide, which has also been started in this country.

The manufacture of electrolytic caustic soda and chlorine has also had a very creditable showing in this country in recent years, and in this connection several American types of cells have been successful. I refer to the Castner electrolytic cell, which has operated successfully for a term of years, and the Townsend cell, of more recent development. By the aid of these inventions it has been made possible to establish at Niagara Falls several flourishing chemical industries and to give an impetus to the movement for the emancipation of the United States from dependence on European chemical manufacture.

I have thus sketched the development and establishment of a number of chemical industries of distinctively American origin. My list is not intended to be an exhaustive one. It could readily have been extended. It is enough, however, to show that we have done very creditably and, in fact, have done much more than is generally known to the public.

As I said in beginning these remarks, "With the wonderful richness of this country in the raw materials which lie at the basis of chemical industries, and with the well-known inventive and mechanical turn of our people, we would be greatly disappointed if we did not find some results in the way of the establishment of new and distinctive lines of manufacture and the production of new products."

So much for the establishment of new industries. However, unless the supply of raw materials is so specially limited to the country as to preclude their becoming available elsewhere, a time will come for an important industry when the manufacture becomes competitive in an international sense. Then a national policy with regard to established industries becomes of the greatest importance. Legislation can foster these industries in a great variety of ways, or it can hamper them so that international competition soon puts them at a disadvantage.

If we are to maintain our chemical manufactures already begun and reach out for a stronger and more independent position in industrial chemistry, the matters of legislation, the tariff, and our patent laws must be given intelligent thought and such action taken as will give us a fair show in the world's competition. As that is a large subject, involving many considerations, I will not enter upon it here.

The U. S. Consul General at Cairo, Egypt, reports that a firm of manufacturing chemists in the United States recently asked for a sample of musenna bark (*Albizzia anthelmintica*), which the firm informed him was indigenous to Kordofan, in the Sudan. He received, upon application to the Sudan Government, samples of the bark from the Director of the Commercial Intelligence branch of the Government at Khartoum. In forwarding these samples, the director informed him that, so far as he was aware, there was no existing trade in this product, but that if any demand for it appeared to be likely he would endeavor to arrange for a supply of the bark, provided details as to price and quantity required were furnished.

AMERICAN POTASH.*

The potash situation for 1915 remains chaotic. The syndicate has apportioned for 1915 425,370 tons of potassium oxide (K_2O) for foreign consumption, but there is little prospect of any considerable tonnage of this apportionment effecting delivery. Potash compounds are still used for the bursting charge in shells, for fulminates, etc., and having thus military value, are properly contraband. However, it is doubtful if any tonnage of moment could be moved, even if the possible military uses were disregarded. The United States must accept a shortage of fertilizer potash for 1915, and very probably for 1916. Further, we must expect greatly increased prices when European trade is again free of obstruction, for potash must bear its full burden of the costs of the war in Europe.

It may be assumed that the potash supply for 1914 was hampered by the outbreak of war. For the ten years ending with 1913, the potash imported into the United States for agricultural uses amounted to 1,822,090 short tons of potassium oxide. Assuming the consumption of 1904 to have been 106,190 short tons (this quantity was imported for agricultural uses in that year), a smoothed curve indicates an average annual gain in potash consumption for the ten years of slightly more than 10 per cent.

For the same period 5,045,740 short tons of phosphoric oxide from phosphate rock were used in fertilizers; and, for 1904, 404,330 short tons. A smoothed curve indicates that the annual increase in phosphoric oxide consumption for the period averaged somewhat less than 5 per cent. These data are shown graphically by the appended diagram.

It is interesting to note the markedly greater increase in potash consumption over phosphoric oxide, especially as the same general relative gain would doubtless be shown for nitrogen were it possible to determine accurately the figures. Among our official agricultural experts are not a few who claim that, except for special soils, the use of potash fertilizer is needless. One cannot pay the farmers of the United States so poor a compliment as to assume this great relative gain for potash is solely due to a propaganda, however effectively same may have been administered; one must conclude that this potash has been used because such use was found profitable. It is true that most soils contain as a natural condition vast quantities of potash, yet it seems to have been found profitable to add to such soils relatively extremely small quantities of soluble potash. The phenomenon seems to rest wholly upon the fact that the soluble potash is "available" to growing plants, while the naturally occurring soil potash is not. This points also to the raw rock phosphate promotion, which has a small measure of official sanction. There is no evidence to show that raw rock phosphate is any more effective in the soil than raw rock potash.

The potassium oxide (K_2O) fertilizer needs of the United States now amount to about 250,000 short tons per year, with an annual increase of about 10 per cent. Market restrictions have considerable bearing on the distribution, and the price limitations are also more or less dominant. The use of potash in fertilizers is not a fad, nor a propaganda-born development; absolutely authentic experimental evidences are not lacking proving its value. Hence, we must have potash. Experience has taught us a source of supply under German control is not dependable. The reported potash deposits in Spain, Austria, etc., are not in commercial evidence; thus far, the efforts of the United States Geological Survey have failed to locate in the United States any potash deposits analogous to those of Germany. It is essential to the agricultural interests that a dependable source of potash supply available to the United States be found, and with little delay.

As possible sources of permanent supply may be mentioned—

(a) Sugar residues.
(b) Portland cement flue dust.
(c) Kelp.
(d) Secondary salt deposits.
(e) The silicate minerals.

SUGAR RESIDUES.

In extracting sugar from cane or beets, a large proportion of the soluble mineral in the cane or beets is extracted with the sugar juice, and upon crystallization of the sugar, remains in the molasses residue. Whether this molasses is used for fermentative processes, or the sugar recovered by means of barium, a final end-product is reached containing the soluble potash, and this end-product is now generally thrown away as waste. Averaging the sugar seasons of 1913 and 1914, the total potassium oxide thus recoverable in the United States will not exceed 30,000 short tons; approximately 60,000 short tons of commercial "muriate." This is a considerable item, but, unfortunately, the lion's share of this potash comes from beet root sugar, and there is no considerable prospect of any marked extension of this industry. In fact, it is safe to assert that beet sugar potash will always be insufficient to replace the potash used in growing sugar beets.

PORTLAND CEMENT RESIDUES FLUE DUST.

The "raw" mixture used in burning cement contains more or less feldspar and other potash bearing silicates. In ordinary practice one barrel of cement is the result of burning 600 pounds of this raw mix. The raw mix contains usually in 600 pounds about 4.8 pounds of potassium oxide, and the resulting barrel of cement contains about 1.8 pounds; hence, in the process of burning the cement approximately 3 pounds of potash per barrel is dispersed as the flue dust, etc. Assuming a recovery of 90 per cent, which is quite practicable, for each barrel of cement made 2.7 pounds of potassium oxide may be recovered. The annual

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*From The American Fertilizer.

Portland cement production of the United States is approximately one hundred million barrels; of this, perhaps, 50 per cent is made from slag, or under conditions precluding potash recovery. Therefore, the prospective potash recovery from cement may be estimated at 67,500 short tons of potassium oxide, or 135,000 short tons of commercial "muriate." This procedure has been somewhat carefully investigated, and the estimates indicate a factory cost of such potash at 34 cents per unit. It has been proposed to enrich the cement raw mix by incorporating a small percentage of feldspar. In many places this plan is practicable, resulting in a potash output more than doubled, and at a cost less than 30 cents per unit.

Potash from cement is an attractive proposition, but has been obscured somewhat by the infliction of a number of commercially hopeless recovery devices. As a result, in 1914, little or no potash was drawn from this source.

KELP POTASH.

This proposition has been widely advocated in the past few years, and has had the advantage of research by government officials. Its field of usefulness is probably confined to the Pacific coast. It is estimated that from conveniently available groves of kelp, from five to six million tons of green kelp may be harvested annually, which, when dried to 10 per cent moisture, would produce 500,000 tons of a product containing 2 per cent ammonia and 16 per cent potassium oxide; say 80,000 tons of potassium oxide. The cost of producing a ton of dried kelp has been estimated at $9.00; as this means harvesting, transporting to mill, drying, and grinding, based upon 10 tons of green kelp, the estimate is obviously very low. A cost of $12 per ton of dry kelp should be ample, and, deducting from this $5.00 as a reasonable value for the organic nitrogen, leaves a cost of $7.00 for 16 units of potash, or approximately 44 cents per unit. Delivered to the Atlantic seaboard, the total costs would probably approximate $18.00 per ton, of which the ammonia value would be $5.00 and the potash cost over 80 cents per unit. If this product is ignited in order to provide a high-grade potash product for shipment via Panama, the product would contain about 40 per cent potassium oxide, which would cost delivered to Atlantic seaboard ports about $30, or about 75 cents per unit. The crude salt could easily be refined at the Pacific coast plant, and thus brought up to 50 per cent potash content, but it is doubtful if any material lessening in cost would be thereby effected.

It is evident that the Pacific coast kelps may be regarded as a tangible source of a very considerable potash supply. Commercially, the project is not very attractive. The renewal of the kelp growth is probably as problematical as that of any other plant, and a systematic harvesting of the plants may possibly so deplete sources of supply convenient to the reducing plant as to make operations commercially impracticable. A number of companies have been organized, and the kelp project has been under exploitation for several years, but no potash of moment has as yet reached the eastern market, and this eastern market consumes more than 90 per cent of our total potash requirement.

SECONDARY SALT DEPOSITS.

This source of potash may be assumed to represent the leachings of potash bearing minerals, and of vegetable matter, accumulated in "countless ages" (more or less), in drainage basins having no outlet, and which are crystallized by means of solar evaporation. These deposits are, practically, invariably very low grade. They contain potash, but in small proportion as compared with other salts. These deposits usually occur in rainless or nearly rainless regions, which in the United States means a large transportation charge to reach a market. It is, of course, necessary to refine the crude salts, and there are few instances in which the extraction of the potash alone is commercially practicable. Except for a severely limited local market, sodium chlorides and sulphates have no commercial value, and sodium carbonate and bicarbonate a very limited market within a practicable transportation cost of the deposits. Borax and potash are capable of bearing the cost of transportation, but these two salts must bear the total cost of refining. To cite an instance, the Searles Lake deposit has been estimated to contain for its 47-foot bed of brine and deposits of salts, in a total weight of eight hundred millions of tons of brine and crystal, over sixteen millions of tons of potassium oxide and some seventeen millions of tons of anhydrous borax. That is, for every ton of potassium oxide prepared for market, somewhat more than a ton of anhydrous borax must also be produced; and some 50 tons of brine and salts treated. The cost of this treatment has been variously estimated, from $1.75 to $2.00 average per ton of brine and crystals. Comparing with similar work in Germany, allowing for vastly more costly conditions at Searles Lake, the maximum cost estimate would probably be exceeded; but, accepting two dollars as the average cost of treating one ton of brine and crude salt crystals, the cost of producing, say, two short tons of 80 per cent muriate of potash (100 units of potassium oxide, and about one ton of anhydrous borax), will be $100. It is evident that the profit margin is very narrow; but it is an assured supply of potash at need. It is necessary to note that the total possible market for Searles Lake borax can hardly exceed 60,000 tons per year; hence, the possible potash output to be expected from this source cannot as a commercial proposition exceed 120,000 tons of 80 per cent muriate, or say 60,000 tons of potassium oxide—less than 25 per cent of our annual needs.

The small alkali lakes in western Nebraska suggest a promising source of potash, as they are within a practicable transportation cost of a market for such by-products as sodium carbonate, chloride, and sulphate. Unfortunately, these accumulations are small, and seriously endanger the plant cost necessary for refining. However, one of these lakes (Jesse Lake) has been extensively examined. According to the report. the total possible potassium output from this lake amounted to about 48,000 tons of commercial potassium sulphate, and allowing the market price for all by-products, the cost of such potash would be about 40 cents per unit. This does not include the heavy plant cost write-off necessary for such a small possible production.

Of quite similar nature are various alunite deposits reported in Utah, Arizona, and Mexico. Alunite is a natural alum, a double sulphate of potash and alumina, and when heated to a high temperature it decomposes to alumina and potassium sulphate. The furnaced residue may then be extracted with water, and the sulphate of potash thus obtained in solution may be concentrated, and the potash salts separated by crystallization.

The mineral alunite contains theoretically 11.4 per cent potassium oxide, and the total operation from mining the mineral to the finished potassium sulphate costs less than $3.00 per ton, unless the cost of water and fuel is high. However, under conditions favorable to alunite occurrence and permanency, both fuel and water are likely to be rather costly, hence the processing costs are apt to be about $5.00 per ton. Also, the mineral does not run true, the run-of-mine product is likely to average nearer 9 per cent potash than 11 per cent. As the by-product alumina contains both iron oxide and silica, it has the value of bauxite, which means that at the site of known extensive alunite deposit it is not worth the freight cost to reach a market. The general evidence is to the effect that alunite as a source of fertilizer potash is commercially impossible.

In general summary, the extraction of potash from secondary salt deposits supplies a known source of potash in quantity ample for our needs for many years to come; but such potash must cost on the farm probably more than the price farmers have been accustomed to pay heretofore.

THE SILICATE MINERALS.

The potash bearing silicates, such as feldspar, leucite, muscovite, etc., occur in immense deposits in various sections of the United States, and run-of-mine rock contains from 9 to 12 per cent potassium oxide. It is to these deposits we must look for cheap potash, in quantity. The number of patented processes for extracting potash from feldspar pass the century mark; most of them are practical technically, but not commercially. An average run-of-mine feldspar will approximate—

Sodium oxide	2	per cent
Potassium oxide	11	"
Alumina	17	"
Silica	68	"
Iron oxide, etc.	2	"

Assuming 95 per cent of the potash is recovered, one short ton of feldspar produces 209 pounds of potash, which, at 3 cents per pound, gives a gross factory value of $6.27. Potash at a higher factory cost than 3 cents constitutes an impracticable commercial condition. Feldspar delivered to the factory, even when the factory is located at the mine, will cost about $1.00, which leaves $5.27 for manufacturing cost, a sum totally inadequate for the vast majority of patented processes. It has been proposed to find a market for the silicate and aluminate waste products, but as one ton of potassium oxide would be accompanied by from 15 to 20 tons of such waste by-product, it is evident that no market for such waste product could sustain any volume of potash production of moment.

Messrs. Cushman and Coggeshall, of the Institute of Industrial Research, of Washington, D. C., give in The American Fertilizer for December 12, 1914, elaborate details of a feldspar potash process, in which calcium chloride, a waste soda ash product, is used as the decomposing agent. The results are those of a carefully conducted research, and are, no doubt, dependable, but the cost of potassium oxide by this process is 3.1 cents per pound, or 62.04 cents per "unit"—a cost price verging sharply upon the limit of commercial feasibility.

A more hopeful prospect would seem to be in the use of feldspar as a substitute, wholly or in part, for the clay used in making Portland cement; but, unfortunately, limestone and feldspar rarely occur closely associated, which implies a heavy freight charge for transporting the spar to the lime. Assuming, however, feldspar delivered to the cement mill at a cost of $3.00 per ton, and an extraction of 80 per cent of the potash and a credit of 50 cents per ton for cement-making material, the cost of recoverable potash per pound would be 1.42 cents per pound. To this must be added the cost of effectively scrubbing all the exit gases of the cement kiln, which implies mechanical draft and the concentration and crystallization of the crude potassium carbonate. The details of such cost estimate are too extensive for reproduction here, but the final conclusions point to a cost per pound of recovered potassium oxide of 1.36 cents, making the total cost 2.78 cents. This procedure, if confirmed, offers an ample supply of fertilizer potash, at a cost on the farm at least not in excess of the period before the present European war. The weak point in this process seems to be the recovery of the volatilized potash. The gases so far as potash content is concerned are of extreme attenuation, and it seems probable that the costs of thoroughly scrubbing same may in practice impose problems not yet thoroughly worked out.

A large number of feldspar extraction processes separate the alkali and alumina as such, having as waste the silica of the spar, together with the small percentage of iron oxide, lime, etc. This latter product would contain at least 95 per cent silica, a purity sufficient for most purposes. To achieve any considerable tonnage of potash, however, the output of this waste silica would be excessive, and on this account a value of only 25 cents per short ton is assigned. The potash in these processes effects a 99 per cent recovery, and the alumina a total recovery. The potash may be valued at the factory at 3 cents per pound, and the alumina basis 100 per cent. Al_2O_3, at 2 cents. Under this schedule, an average feldspar would exhibit a gross factory value of $13.50 per short ton. Against this must be imposed a somewhat extensive series of operations, involving the handling of the spar and its solvents several times, accompanied by at least one fusion, and one extraction by boiling or autoclaving. But, allowing for all these operations, the producing costs should certainly not exceed the gross value of $13.50 per ton of feldspar treated. Of these processes, those which involve the use of an autoclave appear to be the most promising. All of them, practically, involve the phase of converting the silica into alkali silicate, and the separation of the alkali by means of carbon dioxide gases, or by extraction with mineral acids. There are many permutations of these processes, and the patents dangerously interlock. It is very probable that a great deal of money will be wasted through inadequate technical counsel, but this will be only repeating the experience of most other large industries. To illustrate, the use of hydrofluoric acid has been proposed, and extensively researched, yet its commercial exploitation on any considerable scale is obviously hopeless.

A new method of approach has been lately proposed, consisting of an anhydrous double decomposition with feldspar and another salt, producing associate products, all of which are assumed to have a very wide market utilization. This process proposes to make use of the energy involved in decomposing feldspar to simultaneously effect other and commercially valuable reactions.

IN GENERAL SUMMARY.

To the close of 1914, no naturally occurring deposit of soluble potash salts of commercial availability appears to have been discovered. For local use, a few instances appear to be somewhat more than simply promising; but, covering the potash needs of the United States, we are still without material encouragement. The projects covering feldspar decomposition are many, but if anything technically encouraging has been discovered, certainly no patents covering such discoveries have been issued up to the close of 1914. So far as has been disclosed by the trade and technical press, or in promotion literature, excepting solely the new anhydrous double decomposition project, the recovery of potash as a by-product in making Portland cement seems the only substantial hope for American potash.

It is not to be assumed that the large fertilizer interests have neglected potash. In fact, it is known that one of the large corporations has made extensive feldspar researches on a factory scale, and, notwithstanding that over 90 per cent recovery of potash was effected, the process did not give satisfactory end results. It is also known that another of the large fertilizer corporations has researched extensively with secondary salt deposits, and without successful issue. Perhaps it is as well to state that an assured potash process having a factory producing cost of 60 cents per unit, or even 40 cents per unit, cannot be a good investment so long as it is known that the German deposits can profitably produce below those costs. The farmers of the United States are not likely to ask for a tax on potash in order to build up an infant home industry, which, judging from past experience, may need or demand more and more "protection" as it matures. Hence, it may be stated rather safely that no American potash is worthy of investment support which does not provide for a potash cost at need, at Eastern distributing points, such as Boston, New York, Chicago, Cincinnati, Baltimore, Charleston, Savannah, Atlanta, etc., at a cost per unit not in excess of 40 cents. This appears to imply that a potash deposit analogous to that in Germany must be discovered in the Eastern half of the United States, or that a process for working the potash silicates must be discovered such that the potash involved becomes a mere process incident.

So far as has yet been disclosed by the technical world through its press, or by responsible investment literature, the American potash problem remains unsolved; but, substantial progress appears to have been made, and the solution may come almost any day. A great deal of ink has been used to exploit various coal tar dyestuff processes; a business in its total volume worth about ten millions of dollars annually. It is to be hoped that if a suitable potash process arrives, it will be received with more respect and consideration.

The fall trade of 1915 will probably see the total exhaustion of all potash stocks available for fertilizer. Of the very many feldspar processes proposed there is scarcely one of them but is capable of producing potash at a cost perhaps less than one dollar per unit, a sum only one-third of the market price of fertilizer potash at this time (April, 1915). The trouble lies in the fact that with the close of the present war in Europe it is assumed that potash shipments will be immensely resumed, and at approximately the old prices.

German potash salts, in the forms supplied America prior to the war, were imported at the rate of about 2,500 tons daily. It will take years after the war closes to supply bottoms for such tonnage. It is extremely doubtful if the prices of German potash immediately prior to the war will ever be realized again for German potash. Some means must be found to pay the endless debt imposed by the existing war, and potash is one of the few means in the possession of what is now known as the German confederation for transferring more or less of this debt to foreign peoples. It is a perfectly safe assumption that fertilizer potash will not fall below one dollar per unit for many years to come, except under a competition other than that of German or Austrian potash mines. This should enable the complete elaboration of feldspar potash recovery processes in advance of any possible price disturbance of foreign origin.

As a general rule, the feldspar processes will require about two dollars of permanent investment for one dollar in annual products, assuming potash to be valued at 60 cents per unit. The potash market for 1915 and 1916, and probably for several years to follow, will more than double 60 cents per unit; hence, one dollar in permanent investment will represent about one dollar in manufactured products. Assuming an annual fertilizer potash need of 250,000 short tons; to supply same by means of feldspar patosh will require an investment for plant, etc., of $25,000,000.

If the process could be dovetailed with one or more other useful industrial effects, this large sum might be readily found; but, unfortunately, few feldspar processes make any such promise. Therefore, the fertilizer trade must be patient with its leaders. It is not probable that capital can be found at this time for $25,000,000 new indebtedness; but it is to be supposed that a large proportion will be found, and the fertilizer industry will be enabled in a large measure to fulfil its obligations to the soil.

Oil in sand or earth causes it to have a very high resistance to the flow of an electrical current; that is, speaking technically, to have a very high resistivity. Certain valuable ores in the earth cause it to have a very low resistivity. For any particular specimen of earth the resistivity varies with the moisture content. The damage to pipe systems on account of electrolysis by the return current of street railway systems depends, among other things, upon the resistivity of the earth around the pipes and near the tracks. There are, therefore, many reasons why knowledge concerning the resistivity of certain very limited portions of the earth is desired. In a recent publication of the Bureau of Standards, Department of Commerce, a method for measuring earth resistivity which is free from some of the faults of methods which have previously been used is described. The method is particularly adapted to those cases in which it is important that the measurement be made without disturbing the earth, as is necessary where a sample is taken into the laboratory for measurement, and in those cases where the mean resistivity of a fairly large portion of earth, extending to a considerable depth, is investigated.

Swedish exports of pig iron for the first seven months of this year were 143,200 metric tons against 89,000 tons in the same period a year ago. Total exports of iron and steel to Aug. 1, 1915, were 292,500 tons as compared with 233,000 tons to Aug. 1, 1914, an increase of 59,500 tons.

COMMON SENSE ON THE DYESTUFF QUESTION.*

By J. MERRITT MATTHEWS,† PH.D.

The chemist has long been accustomed to misconceptions by the lay mind of things chemical, but in the recent dyestuff propaganda, these misconceptions do not seem to have been confined solely to the layman, but appear also to have extended to many within the profession itself.

The person most interested in the dyestuff question is probably the textile manufacturer, since a large proportion of his business is dependent on an assured supply of dyestuffs suitable to his requirements, yet it is a rare exception to find a textile manufacturer who is at all acquainted with the nature of the dyestuff problem even in its simplest form. He has a hazy notion that dyestuffs are made from coal tar, but this fact generally comprises the entire extent of his information.

To illustrate the naivety of the lay mind in this respect: shortly after the outbreak of the European war and when the importation of dyes was suddenly stopped and everything was in a chaotic condition of uncertainty, a large textile manufacturer in New England telegraphed me to come to Boston. When I had a conference with him I found he had sent for me to arrange for the manufacture of certain dyestuffs he needed; he explained he had a small building at the mill which could be readily adapted to this purpose, and he had already arranged for an option on several tons of coal tar, and it was up to me to show him how to extract the dyestuffs from the coal tar! It required considerable explanation on my part to convince him of the impracticability of the scheme, and even to the present day I think he has a lurking idea that I advised in this manner simply because I was afraid to tackle the job.

I suppose there are many textile manufacturers in the same category as my friend just referred to, who really believe they can put up a small dye plant in their back yard for the protection of their required colors, their only trouble being that they cannot find any chemists of sufficient capability and experience to carry out the work.

Both the technical journals and the daily papers have published so much during the past year concerning the dyestuff situation that there has been brought about among the public a condition which might properly be termed "dyestuff dementia," and as a result, a wave of scientific insanity seems to have swept many would-be dyestuff experts and inventors out into the sea of folly.

Several months ago, one of these inventors who firmly believed he had at last discovered the secret of the German dyestuffs, and had solved the problem of the American dyestuff industry, came to my laboratory with a "sulphur black" he had synthesized. A company was already being organized to exploit it commercially. I was told all the details of its manufacture had been carefully worked out, that it could be manufactured very cheaply—in fact, so cheaply that German sulphur black even at normal prices could not compete with it; its composition of course was a profound secret.

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*From an address delivered Oct. 22 before the Society of Chemical Industry.

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I was given a sample of this Great Invention of the Age and was asked to test out and report on its dyeing properties. As I was rather well acquainted with the gentleman concerned and knew him to be otherwise sane and normal, I was inclined to take his discovery seriously and went about its investigation. How grievously was I disappointed! The so-called sulphur black produced only a slight dirty stain on dyeing, and its chief component turned out to be simply black sulphide of iron. The inventor had received the information that sulphur black was made by fusing something with sodium sulphide and sulphur; he also observed the fact that iron filings fused with sodium sulphide and sulphur produced a black compound which gave a good permanent black on his hands; hence the secret of the sulphur black dyestuff was solved.

Like most chemists interested in this question, I have followed with mingled surprise and chagrin the propaganda advanced by certain "experts" in the daily papers. At first many textile manufacturers placed considerable confidence in these reports and they were lulled into a sense of security in the belief that in a short time all the dyestuffs needed in American industry would be manufactured in this country by new processes much in advance of the antiquated German methods. So radical and preposterous, however, were many of these schemes that even the most hopeful manufacturers began to exercise their common sense, and to realize that the dyestuff problem was not to be solved by any such method of procedure. Fortunately most of the textile trade journals preserved a sane poise in the matter and their editorial criticisms exposed the fallacy of many of the irrational schemes advanced.

In this connection I might say there was one very hopeful dyestuff proposition which was communicated to me privately, and which unfortunately was not brought to the attention of the Government's press bureau. You all know that red is a widely employed color and that naturally red dyes are in great demand and these dyes are now very scarce and bring a high price. A gentleman in New England owns large cranberry bogs and he was aware of the fact that the cranberry contains a large quantity of beautiful red coloring matter, and any housewife in the land will vouch for the fastness of this color when cotton or linen fabrics have been accidentally dyed with it. This gentleman conceived the novel idea of extracting the valuable red dyestuff from the cranberry without interfering with the edible qualities of the luscious berry. This purely American dyestuff was to be known as Cranberry Red and is doubtless destined to take a place of equal rank with that other American dyestuff known as Osage Orange which has been widely heralded by the Government through its bulletins and press reports.

To return, however, to the realms of common sense! Dyestuffs are well known bodies and in general are of definite and well established chemical constitution. The products from which they are made and the general methods of their building-up or synthesis are also well known and clearly established; and to make these dyestuffs, these starting products must be employed and these methods must be adhered to. Radical methods proposed for the production of dyestuffs, either from newly conceived crude materials or by darkly hidden secret chemical processes, must generally be taken as being the harebrained conception of ignorant enthusiasts, or the illegitimate promotion of straightaway fakers.

The only safe way to proceed in the manufacture of dyestuffs is to carefully select those products which it is considered desirable to make, determine the various intermediate materials which it is necessary to use and to proceed about the intelligent manufacture of these. At the present critical time it is folly to endeavor to prepare dyestuffs by new and untried methods of procedure. From a chemical point of view the making of the actual finished dyestuffs themselves is not in general a difficult or complicated problem, provided the proper so-called intermediates are available. Almost any college student with a fair knowledge of chemistry, for instance, can prepare the dyestuff Chrysoidine with little difficulty and even obtain a pure product and a good yield, if he is provided with the necessary aniline and metaphenylenediamine. But, if my intelligent student is simply given the necessary quantity of benzol as a starting point, and had to first make his aniline and phenylenediamine, I am inclined to the opinion that the chrysoidine resulting from his first attempts will be neither of very good quality nor of very high yield.

There are a number of well known and largely used dyes, such for instance as Victoria Blue, which require the use of Michler's ketone in the course of their manufacture. Michler's ketone is quite an aristocrat among dyestuff intermediates as it rejoices in the high-sounding name of tetramethyl-diamido-benzo-phenone. Given a good supply of Michler's ketone, it is comparatively simple to make quite a number of dyestuffs, but like the proverbial rabbit pie, you have first to catch your rabbit before you can hope to bake your pie.

In my opinion, the crux of the entire question as to the establishment of an American dyestuff industry lies in the economical production of the intermediates. The development of our by-product coal tar industry both from gas tars and coke tars apparently assures us a good supply of raw materials or crudes such as benzol, toluol, xylol, naphthalene, and anthracene. Of course, all these products are at a very abnormal price at present owing to the demands for high explosives, but when this demand lessens these prices will readjust themselves to the conditions of the dyestuff and pharmaceutical industries.

But what the dyestuff business needs in order to get on its feet is a supply of the proper intermediates such as aniline, phenol, alpha and betanaphthols and naphthylamines, and their various sulphonic acids; benzidine, dianisidine, sulphanilic acid, Michler's ketone phosgene gas, naphthionic acid, dimethylsulphate, dimenthylamine, diphenylamine, toluidine, tolidine, benzal chloride, benzaldehyde, salicylic acid, etc. These are the products that form the backbone of the industry and their production must be undertaken by organizations capable of commanding large supplies of the coal tar distillates, as well as sulphuric acid, oleum of high strengths, nitric acid, caustic soda, chlorine, acetic acid, etc., and who are conversant with the technique of such processes as sulphonation, nitration, caustic fusion, reduction, methylation, steam and vacuum distillation and other related operations.

The production of intermediates will be a profitable outlet for the coal tar distillates and for the acid and caustic soda plants; it will also, on the other hand, furnish the possibility for the economical production of dyestuffs and related pharmaceutical products in this country in time of peace and for the production of high explosives in time of war.

Any scheme for the establishment of an American dyestuff industry with a view of making us independent in this respect of other nations, in my opinion will be futile if it does not first of all insure the firm and permanent establishment of the manufacture of the various needed intermediates. If a supply of intermediates is assured, the manufacture of dyestuffs follows as a matter of course; on any other basis it will be a hybrid industry, as it has been heretofore; its existence will be precarious and uncertain.

As to the proper means of fostering and protecting these industries in their infancy and upbuilding, this is a problem worthy of the closest study by our political economists. Most certainly a tariff protection in one form or another will have to be given. Personally I am inclined to favor a high specific duty on both intermediates and on the dyestuffs derived therefrom, with more or less ad valorem duty to meet the conditions of each case. Recurring to my former argument, it would seem to me to be foolish to place a high tariff on the dyestuffs alone, for unless these intermediates are manufactured in this country as well as the dyestuffs themselves, we will never be independent of foreign countries, nor can we hope to establish any kind of normal dyestuff industry here until we have first established a normal and efficient manufacture of these intermediates.

At the present time we hear a great deal of talk and discussion concerning military preparedness for defense against the possibility of foreign attack. Of course, there are many different phases of this question to be considered, but, gentlemen, from a chemical point of view we must realize in its fullest significance the all-important fact that unless our Government in some manner or other develops a well established and extensive industry in the coal tar intermediates, all our schemes for military preparedness will be of no avail. Well trained men and the latest types of artillery will be merely idle machines without the necessary high explosive ammunition to render them operative. And the high explosive supply is based in very large degree on the coal tar immediates.

The time factor in starting the manufacture of these chemicals is an important one—at the present moment it is far more important than the efficiency factor. At the present time the factories starting up for the production of coal tar products are in reality emergency measures and their very foundation is based on the fact that they are taking advantage of a very abnormal trade situation. I know there are many textile manufacturers who feel that all these factories of coal tar products have a sort of stranglehold on the situation and are forcing out of it all the profits they can. But there is another side to be considered—these factories which are now making some dye products as well as other factories which are under construction or projection, are in their turn paying abnormally high prices for all their raw materials, for their apparatus, for their machinery, for their labor. The financial interests involved are taking grave risks, for no one positively knows when the war will cease and just what protection the new industries will have after the war, and even if sufficient protection is obtained its continuance for any length of time is a grave uncertainty.

There is also another factor from a manufacturers' point of view—and one which the layman is apt to overlook. In the manufacture of any article, and especially in the foundation of a new enterprise, there is always an involved manufacturing organization and technique to be built up before the article in question can be produced efficiently and perfectly. There is not only a science in manufacturing, but there is also an art, and this latter is only evolved out of practical experience and in the handling of large quantities of materials on a commercial basis. It involves the training of workmen and foremen to do the right thing at the right time—to keep processes and operations moving along continuously with the minimum expenditure of labor and materials.

If, for example, I ask an organic chemist to look into the processes for making methyl violet, he can furnish me a very good scheme on paper, detail the processes of making the various materials needed and final product desired; he can carry out methods in the laboratory and no doubt produce for me a sample of a few grammes of methyl violet. In connection with suitable engineers and constructors we can devise and install the necessary apparatus for making a ton of methyl violet per day. Now to the layman the problem is solved, all that is necessary to do is to go and turn out a ton of methyl violet per day. But to any one who has had any experience in manufacturing, the problem may have been more or less worked out and disposed of—then comes the art of doing it, involving innumerable factors that the scientist has not yet classified in his organized and exact knowledge, and this art can only be acquired in time and in patience.

Under present conditions, of course, dyestuffs can be produced at absurdedly high costs and will find ready buyers, so the enterprise is sufficiently attractive to lead both money and manufacturers into the field. Given a couple of years of continuous manufacturing of staple products and our American factories will have acquired, no doubt, as fine an art of manufacturing such dyes as the German or Swiss factories and other things being equal should be able to sell on a competitive basis. It is in the equalizing of the other factors, the labor, raw materials, methods of selling and competition, etc., that our political economists, our business men and our Government must help.

But outside of any industrial connections or the fostering of any special industry, for its own interests in preparedness for self-defense our Government should see to it that a suitable line of coal tar intermediates is manufactured in this country free from foreign affiliations or control. In whatever way this may be brought about—by tariff, by antidumping laws, by subsidies or by whatever means, let it be the duty of our Government to see that such an industry is established—and then the users of dyestuffs in whatever industry they may be, may rest assured that the manufacture of the finished dyestuffs will soon be an accomplished fact in this country.

Statistics compiled under the supervision of J. D. Northrop, of the United States Geological Survey, show that the quantity of natural gas commercially utilized in the United States in 1914 exceeded that of any previous year in the history of the industry. The quantity produced amounted to approximately 591,866,733,000 cubic feet, valued at $94,115,524, and exceeded by nearly ten billion cubic feet, or almost two per cent, the former record, established in 1913. Increases were credited to New York, Ohio, Oklahoma, Texas, Louisiana-Alabama, Iowa and California, the state last named alone recording a gain of nearly seven billion cubic feet.

The world's output of new platinum in 1914 is placed at 263,453 troy ounces by James M. Hill in a bulletin of the U. S. Geological Survey, "The Production of Platinum and Allied Metals in 1914." Russia furnished 241,200 ounces, Colombia 17,500 ounces and the United States 570 ounces.

POISONS USED IN THE RUBBER INDUSTRY.

Rubber manufacture involves the use of numerous poisonous substances, of which lead salts, antimony pentasulphide, aniline oil, carbon disulphide, and carbon tetrachloride are the most dangerous. The operations involving exposure to these poisons, however, employ but a small proportion of the large number of workers. No women and very few boys are engaged in such operations. A lesser danger is found in the use of coal-tar benzol and of various petroleum products, such as naphtha, benzine, etc. A considerable number of workers, including women and boys, are exposed to the fumes of these compounds. These facts are brought out in an investigation by Dr. Alice Hamilton, of the industrial poisons used in the rubber industry, the results of which have just been published as Bulletin 179 of the Bureau of Labor Statistics of the Department of Labor.

While it was impossible to get complete data as to the frequency of industrial poisoning in the rubber industry, records were secured of no less than 66 cases of lead poisoning which occurred in 1914 among the rubber workers in the United States. Cases were also found of naphtha poisoning, and of poisoning from carbon disulphide, carbon tetrachloride, and aniline oil.

The dangerous nature of some of the compounds used in the rubber industry is not as yet commonly known, so that cases of industrial poisoning may occur without being recognized as such and ascribed to their true cause. Also, in the case of some of the compounds, the symptoms of poisoning may be obscure or may not develop until some time after the exposure has taken place, so that again the resulting harm may not be ascribed to its true cause.

The investigation on which the bureau's report is based covered 35 rubber factories, located in 15 cities or towns in 9 states. Practically every branch of the rubber industry was included among the activities of these factories. As there are many trade secrets in the manufacture of rubber articles, it was impossible to make the investigation as complete as was desired.

It is possible to equip and manage a rubber factory so that exposure to the various industrial poisons will be reduced to an insignificant minimum or wholly eliminated. Relatively little, however, seems to have been done in this direction.

The Swedish State Railway management has purchased from Germany very recently 20,000 tons of coal briquettes and 72,000 tons of coke for locomotive fuel. Mixing about equal proportions of coke and coal briquettes has been a success, especially in Denmark.

THE LABORATORY

SOME EFFECTS OF SELECTION ON THE PRODUCTION OF ALKALOIDS IN BELLADONNA.*

By A. F. SIEVERS.†

INTRODUCTION.

The improvement of many of our important agricultural crops has been brought about by means of plant selection and breeding, and similar methods are being extended to various other fields of plant production in the hope of achieving similar results.

With a few exceptions, the growing of medicinal plants is still in its early stages, and it is a much-debated question whether these plants when cultivated lose any of their therapeutic properties; but with the constantly diminishing supply of many of our important native drug plants cultivation becomes more and more imperative. Also, the quality of some of the drugs on the market has deteriorated to such an extent that improvement is much to be desired, and it is hoped that this may be accomplished through the methods employed by the plant breeder.

Atropa belladonna is an important mydriatic drug, the supply of which has been of such inferior quality in recent years that the Office of Drug-Plant and Poisonous-Plant Investigations has been conducting experiments for some time with special reference to increasing the alkaloidal content of the plant. The first step was to make a general study of the plant with regard to individual variation of the alkaloidal content; then to study the relation of physical and chemical characteristics—the influence of environmental factors, such as climate and soil—and the fluctuations in the alkaloidal content during the growing season. The results of these investigations have already been reported.[1]

SELECTION OF TYPICAL PLANTS.

A number of plants were selected which from the data obtained in the preliminary investigation showed typical alkaloid-producing tendencies. Although only those plants which produce a high percentage of alkaloids are of commercial value, plants of the opposite type, namely, those which produce only small quantities, were also selected, in order to furnish more comprehensive data on the transmissibility of alkaloid-producing characteristics. An enumeration of the individual plants which were selected from the original lot, showing the alkaloidal content of their leaves at the various stages of growth during two seasons, is given in Table I.

TABLE I.—ALKALOIDS IN THE LEAVES OF SELECTED BELLADONNA PLANTS DURING TWO SEASONS, AT ARLINGTON, VA.

		Alkaloidal Content (Per Cent).					
		Stage of Growth, 1911.					
Plant No.	Yield of alkaloids on which selection was based.	First.	Second.	Third	Fourth.	Fifth.	Average.
34	Low	0.335	.....	0.526	0.532	0.200	0.414
3	do	.384	0.375	.277	.549	.451	.407
23	do	....	.348	.354	.487	.425	.403
46	do	.337	.285	.308	.588	.431	.390
13	Medium	.614	.627	.626	.763	.563	.639
12	High	.649	.782	.693	.497	.584	.641
7w	do	.558	.831	.832	.727	.571	.704
6w	do	.596	.879	.925	.711	.722	.766
		Stage of Growth, 1912.					
34	Low	....	0.292	0.320	....	....	0.406
3	do	....	.393	.448	0.448	....	.426
23	do	0.496	.366	.341	....	....	.401
46	do	.418	.334	.480	.483	0.314	.406
13	Medium	.495	.479	.655	.472	.488	.518
12	High	.767	.631	.685	.715	.394	.638
7w	do	.782	.666	.646	.694	.573	.672
6w	do	.847	.747	.882	.804	.558	.768

METHOD OF CONTROLLING POLLINATION.

The flowers of *Atropa belladonna* are normally cross-pollinated and depend principally on insects, such as moths, beetles, and bumblebees, for the transportation of pollen. When insects are excluded the flowers fail to develop and soon drop off, which indicates that natural self-pollination occurs rarely, if at all.

In 1911 a large number of flower buds were inclosed in manila bags in the hope that close pollination would take place, but none of the flowers set seed. However, seeds resulting from the cross-pollination of the individual plants enumerated in Table I were collected and planted in flats in the greenhouse at Arlington, Va., in the following January. Late in April, when the plants from these seeds were about 3 or 4 ins. high, they were transplanted to the field.

In 1912 a second attempt was made to secure seeds from close-pollinated flowers, and in order to insure fertilization the pollen was transferred to the stigmas by hand before the flowers were inclosed. The method of bagging the flower buds used in the previous year again proved ineffectual, since a species of aphis bred in the bags in great numbers and destroyed the young plant tissues. Seeds were obtained from a number of selected plants which had been inclosed in cheesecloth cages, but even within those cages the aphides often multiplied to such an extent as to injure the plant. The seeds from these plants were sown in flats in the greenhouse and the seedlings therefrom transplanted to the field, the same as in 1911.

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*Bulletin No. 306, Bureau of Plant Industry, U. S. Department of Agriculture.

†Chemical Biologist, Drug-Plant and Poisonous-Plant Investigations.

[1] Sievers, A. F. Individual variation in the alkaloidal content of belladonna plants. Journal of Agricultural Research, V. 1, No. 2, p. 129-146, 1913.

FIRST-GENERATION PLANTS FROM CROSS-POLLINATED PARENTS.

The plants from the seed of the cross-pollinated selected individuals in 1911 were transplanted to the field late in April. There were from 6 to 15 individual plants from each parent. These plants made a fairly rapid growth and by mid-summer were in full bloom, but the growth they had made was not sufficient to make possible a picking from each individual plant. A collective sample was therefore secured from each set of individuals derived from the same parent. On Aug. 30, when the berries were partially ripe, the second picking was made. In picking these samples care was taken to get leaves from all the individuals, so that the results of the assay would indicate as nearly as possible the average percentage of alkaloids in the leaves of the individuals. Table II shows the results of the assays.

TABLE II.—ALKALOIDS IN THE LEAVES OF FIRST-GENERATION BELLADONNA PLANTS GROWN FROM CROSS-POLLINATED SELECTED PARENTS AT ARLINGTON, VA.

—-Parent Plant.—		Alkaloidal Content (Per Cent).		
No.	Yield of alkaloids.	First picking.	Second picking.	Average.
34	Low	0.524	0.693	0.609
3	do	.479	.518	.498
13	Medium	.640	.859	.750
12	High	.650	.882	.766
7w	do	.617	1.063	.840
6w	do	.805	1.282	1.043

From Table II it is evident that these first-generation plants displayed largely the characteristic of the parent plants as regards alkaloid production. Plants 7w and 6w merit special attention, their leaves containing more than 1 per cent of alkaloids.

The following season, 1913, these plants were large enough to furnish samples from each individual, and pickings were made at four stages of growth during the season. The first picking was on May 6, before flowering; the second on May 23, when the plants were in full bloom; the third on June 21, when the first berries were developing; and the fourth on Sept. 8, when most of the berries were ripe and much new growth had appeared in the form of shoots and suckers. The season was a very unfavorable one, and the plants made a rather small growth, so that during July and August the leaves were too small and sparse to secure samples. For the purpose of comparison, Table III gives the alkaloidal content of the various samples and the average for the season, the average alkaloidal content of each picking being summarized at the close.

A careful study of Table III reveals the fact that the individual first-generation plants possess in large measure the same alkaloid-producing characteristic as the parent plant. Plant 6w, the richest of the original 59 individual plants under observation for two years, yielded from cross-pollination first-generation plants which were distinctly rich in the first season and again in the second season. Furthermore, the plants of the first generation from the cross-pollinated individuals selected from the original list for low alkaloidal content have shown a decidedly low percentage of alkaloids during each of the two seasons of growth.

In the previous investigation[2] the plants were richest in alkaloids at the first and fourth stages; that is,

TABLE III.—ALKALOIDS IN THE LEAVES OF INDIVIDUAL FIRST-GENERATION BELLADONNA PLANTS AT VARIOUS STAGES OF GROWTH AT ARLINGTON, VA., DURING THE SECOND SEASON, 1913.

	——-Alkaloidal Content (Per Cent).——				
Plant. No.	First stage, May 5.	Second stage, May 23.	Third stage, June 21.	Fourth stage, Sept. 8.	Average for season.
34_1	....	0.316	0.321	....	0.320
34_2	0.516	.473	.312	0.856	.539
34_3	.608	....	.352	.863	.604
34_4	.754	.434	.288	....	.492
34_5	.622	.542	.356	.683	.551
3_1	.538	.366	.430	.523	.466
3_2	.565	.565	.630	....	.587
3_3	.511	.552	.364	.790	.554
3_4	.693	.607	.350	.833	.621
3_5	.513	.477	.533	.767	.573
3_6	.438	....	.392	....	.415
3_7	.412	.415	.504	....	.444
3_8	....	.300	....	....	.300
3_9	....	.479	.702	.782	.654
13_1	....	.255	.459	.934	.549
13_2	....	.365	.596	....	.481
13_3	....	....	.453	....	.453
13_4	.492	.359	.318	.649	.455
13_5	....	.466	.559	.563	.529
13_6	....	....	.470	.733	.601
13_7	....	.341	.552	.766	.553
13_8	....	.349	.664	.792	.601
13_9	.566	.452	.385	.815	.555
12_1	.854	.653	.737	.494	.688
12_2	.480	.516	.661	.717	.594
12_3	.760	.672	.675	.638	.686
12_4	.605	.572	.626	....	.619
12_5	.558	....	.675	.908	.543
12_6	.809	.601	.625	.716	.688
12_7	.750	.608	.582	.574	.529
12_8	.587	.434	.569	.653	.561
12_9	....	....	.389	.549	.469
$7w_1$	....	....	.626	.737	.681
$7w_2$	.835	.550	.507	.759	.663
$7w_3$	.620	.563	.431	.782	.599
$7w_4$	.792	.777	.588	.804	.740
$7w_5$	....	.521	.699	.998	.739
$7w_6$	.674	.721	.567	.663	.656
$7w_7$	.369	.765	.760	....	.631
$7w_8$	....	.291	....	.645	.468
$7w_9$	.714	.389	.544	....	.412
$7w_{10}$	.634	.496	.489	.764	.596
$7w_{11}$	....	.404	.626	.773	.601
$6w_1$	.541	.543	.501	.666	.561
$6w_2$	....	.693	.881	....	.787
$6w_3$	.850	.641	.787	.885	.791
$6w_4$	.866	.516	.529	.856	.692
$6w_5$	.806	.640	.768	.829	.761
$6w_6$	.780	.735	.663	.733	.728
$6w_7$	.739	.917	1.313	.956	.981
$6w_8$	.780	.921	.937	1.020	.915
$6w_9$	.833	.921	.901	.919	.891
$6w_{10}$	.908	.925	.927	.876	.909
$6w_{11}$	.956	.973	.993	.924	.962
$6w_{12}$	.681	.574	.670	.922	.712
$6w_{13}$	1.143	.639	.852	.754	.847

SUMMARY OF ALL INDIVIDUAL PLANTS FROM EACH PARENT.

Average alkaloidal content of leaves (per cent).

		———-Stage of Growth.———				Average for season.
No.	Yield of alkaloids.	First stage.	Second stage.	Third stage.	Fourth stage.	
34	Low	0.625	0.441	0.326	0.800	0.501
3	do	.524	.470	.488	.739	.512
13	Medium	.529	.369	.495	.765	.531
12	High	.679	.573	.617	.662	.597
7w	do	.662	.547	.583	.769	.617
6w	do	.824	.740	.824	.862	.811
Average		.640	.523	.555	.766	....

the stage before flowering and the stages when the berries are ripe. In another season, however, the same plants were found to be richer in alkaloids at the second and fourth stages. In the present investigation we find the greatest percentage of alkaloids at a stage of growth which corresponds to the fourth stage in the previous investigation. It seems, then, further established that the greatest concentration of alkaloids is at the period when the berries are mostly ripe and the leaves small and sparse.

COMPARISON OF FIRST-GENERATION PLANTS FROM CROSS-POLLINATED AND CLOSE-POLLINATED PARENTS.

From the parent plants, 6w and 7w, which yielded the progeny described in the foregoing pages, seeds were obtained in 1912 through both cross and close pollination and planted for the purposes of comparison. Plants 12, 13, 3, and 34 were dead; therefore no seeds could be secured from them. In their stead, seeds were taken from plants 46 and 23, as these were examples of low alkaloid-yielding plants. The seeds were sown in the greenhouse and the seedlings transplanted to the field early in May, 1913. Owing to the hot weather and severe drought the plants made only a fair growth, and only two pickings were secured, the first on Aug. 19, when the plants were in the flowering stage, and the second on Sept. 23, when the berries were in various stages of ripeness. Table IV shows the percentage of alkaloids in the leaves of the individuals from each selected parent.

TABLE IV.—ALKALOIDS IN THE LEAVES OF FIRST-GENERATION BELLADONNA PLANTS FROM CLOSE POLLINATION AND CROSS-POLLINATION OF SELECTED PARENTS AT TWO STAGES OF GROWTH AT ARLINGTON, VA., DURING THE FIRST SEASON, 1913.

	——Alkaloidal content (per cent).——		
Lot and number.	First stage, Aug. 19.	Second stage, Sept. 23.	Average.
Lot 6w, close pollinated:			
1	0.514	0.430	0.472
2	.687	.594	.640
3	.421	.504	.463
4	.834	.886	.860
5	.773	.736	.755
6	.731	.724	.728
7	.689	.745	.717
8	.735	.633	.684
9	.696	.669	.683
10	.745	.658	.702
11	....	....	....
12	.741	.705	.723
13	.687	.613	.650
14	.767	.750	.759
15	.658	.760	.719
16	.703	.722	.713
17	.786	.741	.764
18	.865	.515	.690
19	.557	.715	.636
20	....	.503	....
21	.753	.904	.829
22	.831	.841	.836
23	.433	.562	.498
24	.771	.693	.732
25	.826	.789	.808
26	.843	.799	.821
27	.807	.657	.732
28	.742	.848	.795
29	....	.565	....
30	.794	....	....
31	....	.662	....
32	.690	.974	.832
33	.679	....	....
34	.640	.748	.694
35	.755	.848	.802
36	....	.836	....
37	.674	.526	.600
Average	.672	.701	....
Lot 6w, cross-pollinated:			
1	....	.724	....
2	.609	.555	.582
3	....	.663	....
4	....	.368	....
5	.705	.683	.694
6	.665	.729	.697
7	.557	.729	.643
8	.598	.447	.523
9	.504	.565	.535
10	.688	.729	.709
11	.759	.543	.651
12	.574	.574	.574
13	.594	....	....
14	.693	.550	.622
15	.391	....	....
16	.646	....	....
17	.478	....	....
18	.486	.505	.496
19	.450	....	....
20	.621	.526	.574
21	.535	.726	.681
23	....	.613	....
Average	.586	.602	....
Lot 7w, close pollinated:			
1	.717	.591	.654
2	.645	.545	.595
3	.632	.515	.574
4	....	.394	....
5	.526	.468	.497
6	.654	.658	.656
7	.442	.492	.467
8	.591	.646	.619
9	....	.602	....
10	.409	.550	.480
11	.427	.470	.449
12	.510	.586	.548
13	.685	.753	.719
14	.650	.712	.681
15	.340	.626	.483
16	.626	.705	.666
17	.492	.633	.563
18	.696	.715	.706
19	.478	.669	.574
20	.521	....	....
21	....	....	....
22	.829	.894	.862
23	.574	.515	.545
24	.717	.940	.829
25	.813	.856	.835
26	.730	.641	.686
Average	.595	.632	....
Lot 7w, cross-pollinated:			
1	.526	.771	.649
2	.448	.468	.458
3	.681	.586	.634
4	....	.369	....
5	.512	.678	.595
6	.813	.885	.849
7	.430	.621	.526
8	.658	.669	.664
9	.676	.468	.572
10	.646	.646	.646
11	.741	.631	.686
12	....	.736	....
13	.598	.635	.617
14	....	.621	....
15	.646	.799	.723
16	.675	.526	.601
17	.729	.633	.681
18	.669	.609	.639
19	.681	.511	.596
20	....	.369	....
21	.504	....	....
22	....	....	....
23	.609	....	....
24	.500	....	....
Average	.618	.611	....
Lot 23, cross-pollinated:			
1	.199	....	....

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[2] Sievers, A. F. Op. cit.

2	.369		
3	....		...
4	.426		...
5	.305		....
6	.332	..	..
7	.491	..	..
8	.538		..
9	.455		....
10	.393	...	....
Average	.408	.	...
Lot 46, cross-pollinated.			
1	.383	.406	.395
2	.369	.382	.376
3	.451	.480	.466
4	.314	....	....
5	.528	....	....
6	.480	.711	.611
7	.400	.366	.383
8	.332	.316	.324
Average	.407	.448	....

SUMMARY OF AVERAGES FOR THE VARIOUS LOTS.

Lot.	Alkaloidal yield of parent.	Average alkaloidal content (per cent). First stage.	Second stage.	Season.
Lot 6w, close pollinated	High	0.672	0.701	0.686
Lot 6w, cross-pollinated	do	.586	.602	.594
Lot 7w, close pollinated	do	.595	.632	.614
Lot 7w, cross-pollinated	do	.618	.611	.615
Lot 23, cross-pollinated	Low	.408	....	.408
Lot 46, cross-pollinated	do	.407	.448	.428

The following year, 1914, these plants were again analyzed. The first picking was made on Aug. 1, when the berries were beginning to ripen. This is the stage at which, as shown by other experiments, the greatest percentage of alkaloids is present. The second picking was made on Sept. 5, when the berries had all ripened. Table V shows the percentage of alkaloids in each case, the averages being summarized at the close.

TABLE V.—ALKALOIDS IN THE LEAVES OF FIRST-GENERATION BELLADONNA PLANTS FROM CLOSE POLLINATION AND CROSS-POLLINATION OF SELECTED PARENTS AT TWO STAGES OF GROWTH AT ARLINGTON, VA., DURING THE SECOND SEASON, 1914.

Lot and number.	Alkaloidal content (per cent). First stage, Aug. 1.	Second stage, Sept. 5.	Average.
Lot 6w, close pollinated:			
1	0.864	0.882	0.873
2	.770	.611	.690
3	.746	.581	.663
4	.858	.858	.858
5	.771	.829	.800
6	.761	.956	.858
7	....	.924	....
8	.921	.854	.889
9	.916	.864	.890
10	.859	.618	.738
11	....	....	....
12	1.045	.953	.999
13	....	.831	....
14	....	....	....
15	.646	.693	.669
16	....	....	....
17	.739	.795	.767
18	.913	.612	.627
19	.930	.708	.819
20	.681	.882	.781
21	.935	.813	.874
22	1.016	.747	.881
23	....	.777	....
24	1.193	.753	.973
25	.969	.837	.905
26	.990	.833	.911
27	1.103	.699	.856
28	.976	.691	.833
29	.797	.599	.698
30	.911	.742	.841
31	1.030	.783	.906
32	.902	.792	.847
33	1.031	....	....
34	1.096	.908	1.002
35	1.043	.765	.904
36	.860	.657	.908
37	.744	.451	.549
Average	.906	.765	....
Lot 6w, cross-pollinated:			
1	....	.753	....
2	1.169	.687	.923
3	.969	.717	.813
4	....	....	....
5	1.074	.756	.915
6	.990	.575	.782
7	.987	.530	.758
8	....	....	....
9	.790	.565	.677
10	.804	.663	.733
11	1.062	.647	.854
12	.771	.712	.741
13	.943	.626	.784
14	.903	.572	.737
15	.810	.657	.733
16	....	....	....
17	.929	....	....
18	.728	.621	.674
19	.997	.520	.758
20	....	.559	....
21	1.121	.664	.884
22	1.138	.608	.873
Average	.952	.634	....
Lot 7w, close pollinated:			
1	.948	.771	.859
2	.626	.672	.649
3	.898	.693	.795
4	....	.777	....
5	.704	1.098	.906
6	.953	.777	.865
7	.624	.594	.609
8	.851	.834	.842
9	.756	.926	.841
10	.927	.822	.874
11	....	.873	....
12	.950	.657	.803
13	.744	.762	.753
14	1.193	.837	1.015
15	.997	.599	.798
16	.882	.809	.845
17	.997	.632	.811
18	.694	.707	.650
19	.964	....	....
20	.709	....	....
21	1.010	....	....
22	.797	....	....
23	.810	.687	.748
24	.790	.651	.665
Average	.855	.753	....
Lot 7w, cross-pollinated:			
1	.992	.672	.832
2	1.062	....	....
3	.864	.596	.730
4	.810	.523	.666
5	.911	.553	.732
6	1.036	.696	.866
7	.568	.463	.515
8	.816	....	....
9	1.062	.596	.579
10	.690	....	....
11	.868	....	....
12	.838	....	....
13	1.062	.574	.818
14	.990	.672	.831
15	.758	.425	.591
16	.885	.641	.763
17	.704	.535	.619
18	.983	....	.983
19	.739	.394	.566
20	.758	.897	.827
21	1.015	.732	.873
22	.784	.813	.798
23	.872	.620	.746
24	.877	.798	.838
25	1.036	.823	.929

26	1.036	.823	.929
27	.631	.345	.488
Average	.865	.619	....
Lot 3:			
1	.452	.319	....
2	.452	.528	....
3	.306	.681	....
4	.425	.365	....
Average	.409	.473	....
Lot 23:			
1	....	.344	....
2	....	.472	....
3	....	.517	....
4	....	.532	....
5	....	.448	....
6	....	.581	....
7	....	.505	....
8	....	.588	....
9	....	.502	....
10	....	.487	....
Average	....	.497	....

SUMMARY OF AVERAGES FOR THE VARIOUS LOTS.

Lot.	Alkaloidal yield of parent.	Average alkaloidal content (per cent). First stage.	Second stage.	Season.	
Lot 6w, close pollinated	High	0.906	0.765	0.835	0.814
Lot 6w, cross-pollinated	do	.952	.634	.793	
Lot 7w, close pollinated	do	.855	.753	.804	.773
Lot 7w, cross-pollinated	do	.865	.619	.742	
Lot 3, cross-pollinated	Low	.409	.473	.441	
Lot 23, cross-pollinated	do	....	.497	.497	

From Tables IV and V it becomes apparent that during both the first and second seasons these first-generation plants display very markedly the characteristic of the parents as regards alkaloid production. Thus, in 1913 the average percentage of alkaloids found in the plants from the original parent 6w and the parent 7w, which were selected for high alkaloid-producing tendencies, was 0.640 and 0.615 per cent, respectively. On the other hand, the averages from the plants 23 and 46, which were produced from parents of the opposite tendencies, are 0.408 and 0.428 per cent, respectively. Again the following year we find the average of plants 6w and 7w to be 0.814 and 0.773 per cent, respectively. Lot 46 was not picked that year, but lot 23 averaged 0.497 per cent.

It will be seen from the tables that the effect of close pollination as compared with cross-pollination is not as great as would be expected. In the case of 6w the plants from close pollination are on the average 0.091 per cent richer than those from cross-pollination in 1913, and 0.042 per cent richer in 1914. The 7w plants show a difference of 0.001 per cent in favor of cross-pollination in 1913 and a difference of 0.062 per cent in 1914. Sufficient information has not been obtained to indicate with any degree of certainty the influence of cross-pollination and close pollination on the transmissibility of the alkaloid-producing characteristic. As a possible explanation of the large percentage of plants with high alkaloidal content among the first-generation plants secured from cross-pollinated selected parents, Dr. W. Van Fleet, of the Office of Drug-Plant and Poisonous-Plant Investigations, has prepared the following statement:

> The arrangement of anthers and stigma in the belladonna bloom and the respective periods of their maturity and receptivity are such as to fit the plant in a high degree for cross-pollination and to almost exclude the probability of close fertilization in individual flowers. However, the feeding habits of the principal pollinating insects (mostly night and day flying lepidoptera), which visit in turn may open blooms on the same plant, may tend after all to promote self or close pollination on a considerable proportion of blooms on any given plant. If all the seeds in a single fruit should mature and produce plants with a high alkaloidal content or any other transmissible feature of the seed parent, it does not necessarily follow that the pollen of another individual possessing this feature in a lesser degree might not have a reducing effect on the desired characteristic, as the seeds planted may easily be the result of actual close pollination between different blooms of the maternal plant or even of self-fertilization of an individual bloom. It is but fair to suppose that a majority of the seeds of a given plant may thus be self-pollinated, notwithstanding nature's adaptation of the blooms for crossing, unless it has been made apparent that belladonna blooms are not receptive to their own pollen or to that of flowers on the same plant, but must be fertilized by pollen produced by another individual. This conclusion has not been demonstrated by any controlled experiments that have come to my knowledge.

SECOND-GENERATION PLANTS FROM CROSS-POLLINATION.

Up to this point the investigation has dealt entirely with first-generation plants. During the season of 1914 analyses were made of plants which represented the second generation of the original selected individuals. The seed which furnished these plants was secured from the following first-generation plants in the fall of 1913: $6w_7$, $6w_{10}$, $6w_{11}$, $7w_5$, 2_2, 2_3, 3_1, 3_6, 3_7, 34_2, 34_3, 34_4, 35_5. The plants from 6w and 7w were selected as types of high alkaloid-yielding plants, those from 2 as medium, and those from 3 and 34 as low alkaloid-yielding types. The seed was planted in the greenhouse at Arlington, Va., in January, 1914, and the plants were transferred to small pots when of suitable size.

TABLE VI.—ALKALOIDS IN THE LEAVES OF SECOND-GENERATION BELLADONNA PLANTS FROM CROSS-POLLINATED PARENTS AT TWO STAGES OF GROWTH AT ARLINGTON, VA., AND MADISON, WIS., IN 1914.

Lot and number.	Arlington, Va. First stage, Aug. 18.	Arlington, Va. Second stage, Sept. 12.	Arlington, Va. Avge.	Madison, Wis. First stage, Aug. 4.	Madison, Wis. Second stage, Sept. 5.	Madison, Wis. Avge.
Lot $6w_7$:						
1	0.783	0.461	0.622	0.962	0.956	0.959
2	.542	.570	.556	.707	.813	.760
3	....	.488	.488	....	.781	.781
4	.791	.666	.728	.653	.653	.653
5	.414	.558	.486	.791	.530	.710
6	....	.851	.851	.765	.707	.736
7	.574	.620	.597	.580	.791	.685
8	.716	.646	.681	.599	.861	.730
9	.837	.835	.836	.794	.583	.688
10	.554	.653	.603	.478	.461	.470
11	.708	.522	.615	1.020	.727	.873
12	.674	.340	.557	1.322	1.027	1.174
13	.695	.605	.650	.867	.813	.840
14	.588	.669	.628	.956	.908	.932
15	....	.525	.525	.538	.949	.793
Lot $6w_{10}$:						
1	.669	.541	.605	.736	.557	.646
2	.755	.691	.723	.653	....	.653
3	.639	.516	.577	.685	.829	.757
4	....	....	....	.806	.759	.783
5	.641	.573	.607	.822	1.068	.945
6	.550	.541	.546	.762	.876	.819
7	.748	....	.748	.740	.813	.776
8	.557	....	.557	.803	.733	.768
9	....	....	....	1.062	.908	.985
10	.327	.398	.362	.695	.838	.766
11	....	....	....	.905	1.115	1.010
12	....	....	....	.752	.813	.783
13	....	....	..	.775	.943	.859
14	....	....	.. .	.554	.605	.579
15	....	....	....	.806	.752	.779

TABLE VI.—ALKALOIDS IN THE LEAVES OF SECOND-GENERATION BELLADONNA PLANTS FROM CROSS-POLLINATED PARENTS AT TWO STAGES OF GROWTH AT ARLINGTON, VA., AND MADISON, WIS., *in* 1914.—(Continued.)

Lot and number.	Arlington, Va. First stage, Aug. 18.	Arlington, Va. Second stage, Sept. 12.	Arlington, Va. Avge.	Madison, Wis. First stage, Aug. 4.	Madison, Wis. Second stage, Sept. 5.	Madison, Wis. Avge.
Lot $6w_{11}$:						
1	....	....	....	.554	.488	.521
2	.557	....	.557	.573	....	.573
3	.630	.636	.633	.580	.759	.669
4	.597	.504	.547	.781	.749	.765
5	....	....	....	.630	....	.630
6	.800	.583	.692	.959	.988	.973
7	.840	.513	.676	.914	.908	.911
8	....	.701	.701	....	....	....
9	....	....	....	....	....	....
10	....	.408	.408	....	....	....
11	.359	.541	.450	....	....	....
12	....	....	....	....	....	....
13	....	.392	.392	....	....	....
14	.574	.775	.679	....	....	....
15	....	....	....	....	....	....
16	....	.488	.488	....	....	....
17	.587	.433	.510	....	....	....
18	.526	.318	.422	....	....	....
Lot $7w_5$:						
1	.653	.653	.653	.521	.560	.551
2	.659	.557	.608	.513	.484	.498
3	.543	....	.543	....	....	....
4	.554	.541	.548	....	....	....
Lot 2_2:						
1	.545	....	.545	.580	.775	.677
2	.365	.408	.386	1.170	1.221	1.196
3	.369	.494	.431	.864	.723	.794
4	.310	.478	.394	.765	.617	.691
5	....	.295	.295	....	.605	.605
6	.557	.513	.535	.642	1.099	.870
7	....	.324	.324	....	....	....
8	.426	.337	.382	....	....	....
Lot 2_3:						
1	....	....	....	.461	.669	.568
2	....	....	....	.478	1.086	.782
3	.573	.547	.560	.573	1.250	.911
4	....	....	....	.620	.535	.577
5	.423	.372	.397	.870	1.309	.589
6	....	.382	.382	.625	.972	.799
7	.489	.646	.567	.478	.924	.701
8	....	....	....	.532	.679	.605
9	.536	.532	.534	.478	.781	.629
10	.462	.455	.459	.491	.636	.564
11	.418	.538	.478	.455	.691	.573
12	....	.382	.382	.510	.924	.717
13	.511	.420	.465	.494	.599	.547
14	.519	.442	.482	....	.892	.892
15	.420	.567	.494	.630	.723	.676
16	.456	.525	.492	.324	.366	.345
17	.510	.318	.414	....	....	....
Lot 3_1:						
1	....	....	....	.474	.617	.546
2	.532	....	.532	.318	.669	.493
3	....	....	....	.312	.423	.367
4	.522	.510	.516	.350	.510	.430
5	....	....	....	.501	.803	.654
6	.197	....	.197	.541	.852	.697
7	.433	.263	.348	.445	.510	.477
8	....	....	....	....	....	....
Lot 3_6:						
1	....	.292	.292	.350	.424	.387
2	....	....	....	.484	.502	.493
3	....	....	....	....	.682	.682
Lot 3_7:						
1	.457	.350	.403	.488	....	.488
2	.502	.324	.413	.717	.978	.847
3	.412	.334	.373	.494	.539	.516
4	.420	.414	.417	.573	.630	.601
5	....	....	....	.653	....	.653
6	.444	.408	.426	.717	.813	.765
7	.448	.636	.542	.488	.672	.580
8	.463	.455	.459	...	.701	.701
9	.452	.550	.501	....	....	....
10	.421	.318	.369	....	....	....
Lot 34_2:						
1	.621	....	.621	.940	.707	.823
2	....	....	....	.729	.646	.687
3	.630	....	.630	.822	....	.822
4	.646	....	.646	.478	.439	.458
5	....	....	....	.797	.605	.701
6	....	....	....	.663	.445	.554
7	.440	.350	.395	.605	.510	.558
8	.562	.376	.479	.756	.845	.800
9	.369	.366	.368	.636	.669	.652
10	.430	.254	.342	.717	.749	.733
11	.459	.382	.421	.710	.886	.798
12	.507	.343	.425	.797	.541	.669
13	.483	.461	.472	.714	.663	.689
14	.521	....	.521	.599	.797	.698
15	.720	.626	.673	.685	.876	.782
16	.550	.461	.505	.302	.701	.501
17	.618	.324	.471	....	.491	.491
18	.511	.382	.447	....	....	..
Lot 34_3:						
1	....	.546	.546	.596	.832	.714
2	.659	.589	.624	.532	.765	.648
3	.650	.501	.576	.573	.791	.682
4	.626	.580	.603	....	.876	.876
5	....	....	....	.559	.803	.681
6	....	....	....	.593	.861	.727
Lot 34_4:						
1	.482	.356	.419	.414	.681	.547
2	.641	....	.641	.350	.752	.556
3	.503	.504	.504	.350	.532	.441
4	.450	.142	.296	.398	.508	.453
5	.489	.458	.474	.461	....	.461
6	.515	.593	.554	.471	.478	.475
7	....	....	....	....	.699	.699
8	.517	.330	.424	.346	.792	.569
9	....	....	....	.359	.732	.596
10	.512	.494	.503	.455	.756	.605
11	.458	.438	.458	...	....	...
12	....	....	....	....	....	...
13	.398	....	.398	....	....	..
Lot 34_5:						
1	....	.461	.461	.398	.414	.406
2	....	....	....	.445	.541	.493
3	.558	.445	.501	.484	.605	.545
4	....	.458	.458	.414	.541	.478
5	....	.343	.343	....	.478	.478
6	...	.478	.478	.541	.911	.726
7	.421	.445	.433	.392	.956	.674
8	....	.318	.318	.583	.573	.578
9	....	....	....	....	.350	.350
10	....	....	....	.414	.468	.441
11	....	....	...	....	.318	.318
12	....	..	....	....	....	....
13	....	....	....	....	....	
14	.674	.532	.603	....	....	..
15	.263	.308	.286	....	....	..

SUMMARY OF AVERAGES FOR EACH LOT, INCLUDING RESULTS, AT TIMMONSVILLE, S. C.

Lot.	Alkaloidal content (per cent). Arlington, Va. First stage, Aug. 18.	Arlington, Va. Second stage, Sept. 12.	Arlington, Va. Average.	Madison, Wis. First stage, Aug. 4.	Madison, Wis. Second stage, Sept. 5.	Madison, Wis. Average.	Timmonsville, S. C. First stage.	Timmonsville, S. C. Average.
Lot $6w_7$	0.656	0.600	.....	0.783	0.777	.....	0.992	.....
Lot $6w_{10}$	.611	.543	.....	.800	.829	.....	.906	.....
Lot $6w_{11}$	.608	.524	.....	.729	.745	.....	.849	.....
Average	.625	.556	0.592	.771	.784	0.778	.916	0.916
Lot $7w_5$	.602	.584	.593	.524	.532	.528	.950	.950
Lot 2_2	.429	.407	.....	.822	.840	.....	.....	.....
Lot 2_3	.483	.471	.....	.674	.814	.....	.771	.....
Average	.456	.436	.446	.748	.827	.788	.771	.771
Lot 34_2	.538	.384	.....	.673	.661	.....	.801	.....
Lot 34_3	.645	.554	.....	.696	.821	.....	.852	.....
Lot 34_4	.496	.414	.....	.530	.660	.....	.663	.....
Lot 34_5	.479	.421	.....	.514	.569	.....	.705	.....
Average	.539	.443	.491	.603	.678	.642	.755	.755
Lot 3_1	.496	.386	.....	.524	.627	.....	.702	.....
Lot 3_6	.....	.....	.....	.476	.536	.....	.532	.....
Lot 3_7	.446	.421	.....	.602	.722	.....	.669	.....
Average	.471	.402	.437	.534	.628	.581	.634	.634

When the plants were about 3 inches high they were divided into three lots. One lot was transplanted to the gardens at Arlington, Va., another lot was shipped to Timmonsville, S. C., and a third lot to Madison, Wis. The object was to grow at these widely separated locations under different soil and climatic conditions plants which were obtained from a definite source. Data would thus be secured which would serve to indicate whether the transmissibility of the alkaloid-producing quality would be affected by external influences. Furthermore, it would throw some light on the question of alkaloid production as dependent on sunlight, rainfall, and soil conditions, which is a question still unsettled. At Arlington and at Madison two pickings were made of all the individuals, while at Timmonsville only one collective sample was secured from the plants from each individual parent. In Table VI the percentage of alkaloids in the individual plants at Arlington and Madison is presented, the summary of averages and the results from Timmonsville being added at the close.

A study of Table VI will reveal the fact that the plants showed marked differences in the percentage of alkaloids produced at the different stations. Thus, the general seasons average of all the plants at Arlington was 0.512 per cent, at Madison 0.663 per cent, and at Timmonsville 0.804 per cent. At the last mentioned station, however, only one picking was made, which may account in some measure for the unusually high percentage of alkaloids found. At Arlington the first picking assayed considerably higher than the second, while at Madison the second picking was richer. It should be remembered, however, in this connection, that the season at Madison is somewhat later than at Arlington. Previous experiments have shown that the plants are richest in alkaloids when the flowering period is over and the berries are beginning to ripen. At this stage the leaves are small but very rich in alkaloids. At Arlington the first picking was made August 18, when the plants were in the stage just described, and the second picking was made later in the season, when the new growth had reduced the percentage of alkaloids considerably. At Madison, on the other hand, the first picking was made Aug. 4, before the rich stage was reached, and consequently the second picking, Sept. 5, corresponds very closely to the first picking at Arlington in so far as the stage of growth is concerned. It is evident from the results obtained that at all three stations these second-generation plants show the characteristics of the parents as regards their alkaloidal content. Naturally, there are individual variations, and the plants at one station may be unformly lower in alkaloidal content than at another station, but the point to be observed here is that at all the stations it is true in a general way that the plants selected originally from parents of high alkaloidal-yielding tendencies show generally a greater percentage of alkaloids than those from parents of the opposite tendency. Table VI shows this very plainly. It must be pointed out, however, that only a few plants were included under lot $7w_5$, and this must be borne in mind when studying the averages.

In order to gather some information regarding the influence of climatic conditions upon alkaloid production, a tabulation was made of the principal weather characteristics at or near the three stations for the four months, May to August, inclusive, of the year 1914. This compilation is shown in Table VII.

TABLE VII.—TEMPERATURE, PRECIPITATION, AND DAYS OF SUNSHINE AT ARLINGTON, VA.; MADISON, WIS., AND TIMMONSVILLE, S. C., DURING MAY, JUNE, JULY, AND AUGUST, 1914.

Station and month.	Temperature (° F.)			Precipitation.			Aspect of sky (days).		
	Mean maximum.	Mean minimum.	Mean.	Total.	Departure from normal.	Days with 0.01 or more.	Clear.	Partly cloudy.	Cloudy.
Washington, D. C.:[1]				Ins.	Ins.				
May	78	55	67	1.72	—2.1	7	14	11	6
June	84	64	73.8	6.20	2	11	12	12	6
July	85	67	75.9	2.32	—2.3	12	7	12	12
August	86	66	76.4	6.00	1.6	10	10	13	8
Total	..	..	..	16.24	....	..	43	48	32
Florence, S. C.:[2]									
May	87.2	57.4	72.3	1.70	....	2	14	13	4
June	92.1	68.9	80.5	3.88	....	7	12	12	6
July	92.8	68.5	80.6	3.31	....	6	12	16	3
August	89.9	69.3	79.6	4.19	....	10	8	15	8
Total	....	....	....	13.08	....	..	46	56	21
Madison, Wis.:									
May	69.7	50.9	60.3	5.97	2.35	13	9	14	8
June	75.7	57.6	66.6	3.46	—0.64	14	8	12	10
July	83	64.6	73.8	1.49	—2.50	8	13	13	5
August	79.6	61	62.5	3.60	.39	7	11	12	8
Total	....	....	....	14.52	.....	..	41	51	31

[1] The conditions at Washington should approximate very closely those at Arlington, Va.

[2] About 7 miles from Timmonsville, S. C.; volunteer observer.

It has been claimed by some investigators that dry and sunny seasons will result in greater alkaloid production than wet and cloudy seasons. The data in Table VII will serve to throw some light on this point. The plants from the three localities specified were all grown from the same seed, and it would appear that if the contention regarding climate were correct there should be some correlation between the quantity of alkaloids found and the seasonal conditions. However, in the four months there is a difference of only about 3 inches in the rainfall and a difference of only five in the number of sunny days. It is true that at Timmonsville the precipitation was the least and the number of sunny days the greatest, and the percentage of alkaloids was also the greatest. It has already been pointed out, however, that only one picking of leaves was secured at this place, which may account for the high average percentage of alkaloids found; and, furthermore, the difference in climatic conditions is so small that little significance can be attached to it. It is possible, of course, that differences in soil conditions at the three stations may be sufficiently great to influence any relationship due to climatic conditions which might otherwise be apparent.

REPRODUCTION OF SELECTED PLANTS FROM CUTTINGS.

In the fall of 1913 cuttings were secured from the first-generation plants and rooted in the greenhouse. Although the season had been bad and the condition of the cuttings was rather poor, a good percentage of them rooted and by spring furnished plants 3 to 4 inches high. These were transplanted to the field early in May. The severe drought during that month caused a considerable number of the plants to die, although they had developed a good root system. On Aug. 18, when the flowering was mostly over, the first picking was made. On Oct. 12, after most of the berries were ripe and some new leaves had developed, a second picking was secured. In Table VIII are given the percentages of alkaloids found in each individual plant, the summary of seasonal averages being added at the close.

TABLE VIII.—ALKALOIDS, AT TWO DIFFERENT STAGES, IN THE LEAVES OF BELLADONNA PLANTS GROWN FROM CUTTINGS FROM SELECTED PARENTS AT ARLINGTON, VA.

Lot and number.	Alkaloidal content (per cent). First stage, Aug. 18.	Second stage, Oct. 12.	Average for season.
Lot $6w_1$:			
5	0.573	0.491	0.532
Lot $6w_2$:			
2	.512	.525	.517
Lot $6w_3$:			
1	....	.525	.525
2	.725	.593	.659
3	....	.496	.496
4	.606	.620	.613
5	.604	.488	.546
6	.837	.749	.493
Average	.693	.578	.634
Lot $6w_4$:			
1	.573	.522	.548
2	.615	.580	.597
3	.585	.343	.464
4	.607	.478	.543
5	....	.589	.589
5	....	.315	.315
7	.573	.442	.508
8	.516	.372	.444
Average	.575	.455	.565
Lot $6w_8$:			
1	.795	.797	.796
2	.745	.749	.747
Average	.770	.773	.772
Lot $6w_9$:			
6	.770	.516	.643
Lot $6w_{10}$:			
1	.623	.618	.621
3	.660	.691	.676
Average	.641	.654	.648
Lot $6w_{11}$:			
1	.771	.653	.714
2	.602	...	.602
5	.598	....	.598
6	.682	.752	.717
8	.661	.775	.718
9	.602	.613	.608
11	.871	.669	.770
12	.801	.829	.815
13	.680	.420	.550
15	...	.630	.630
16	.510	.238	.374
17	..	.537	.537
19	.665	....	....
Average	.687	.611	.619
Lot $6w_{12}$:			
2	.624	.610	.617
3	.731	.398	.565
4	...	.445	.445
Average	.677	.484	.581
Lot $7w_3$:			
2	.477	.429	.453
5	...	.794	.794
Average	.477	.611	.544
Lot $7w_4$:			
1	.587	.567	.577
2	....	.557	.557
3	.562	.525	.544
5	.631	.666	.648
6	....	....	....
7	.436	.669	.553
Average	.553	.597	.575
Lot $7w_5$:			
1	....	.569	.569
2	....	.636	.636
4	.584	.784	.684
5	.837	.759	.798
6	.734	.620	.677
7	.639	.700	.669
8	.657	.578	.668
Average	.690	.664	.677
Lot $7w_{10}$:			
3	.516	.688	.602
6	....	.864	.864
Average	.516	.776	.646
Lot 34_2:			
1	....	.636	.636
3	.499	.391	.445
4	.598	.525	.562
5	.558	.408	.483
6	.601	.590	.596
Average	.561	.510	.537
Lot 34_3:			
1	.623	....	.623
2	.539	.596	.567
Average	.581	.596	.588
Lot 34_5			
1	.514	.439	.476
2	.458	.440	.449
Average	.486	.440	.463

SUMMARY OF SEASONAL AND GROUP AVERAGES.

Lot.	Alkaloid yield of parent.	Average alkaloidal content (per cent). For season.	For all plants from same parent.
Lot $6w_1$	High	0.532	0.616
Lot $6w_2$	do	.517	
Lot $6w_3$	do	.634	
Lot $6w_4$	do	.565	
Lot $6w_8$	do	.772	
Lot $6w_9$	do	.643	
Lot $6w_{10}$	do	.648	
Lot $6w_{11}$	do	.649	
Lot $6w_{12}$	do	.581	
Lot $7w_3$	do	.544	0.610
Lot $7w_4$	do	.575	
Lot $7w_5$	do	.677	
Lot $7w_{10}$	do	.646	
Lot 34_2	Low	.537	0.529
Lot 34_3	do	.588	
Lot 34_5	do	.463	

Here, again, the plants from lots 6w and 7w show marked superiority over those of lot 34, the parent plant of which was poor in alkaloids. These plants will be observed and studied carefully through another season, to determine whether the same relationship holds true, after which desired individuals will be selected and further propagated through cuttings.

CONCLUSIONS.

It having been established in the previous investigation that a wide range of variation exists in the alkaloidal content of belladonna plants, the present investigation was undertaken to determine whether the characteristic of alkaloid production is transmissible to the progeny through seed and whether the character is changed by vegetative propagation. The results thus far show that the first-generation plants secured from seed of cross-pollinated selected individuals display the characteristic of the maternal parent with regard to alkaloid productivity. This condition is generally true at all stages of growth during a season and also for at least two successive seasons. Close pollination of the parent plant has shown only a moderate influence on the transmission of this characteristic.

Second-generation plants from cross-pollination have been grown at Arlington, Va., Madison, Wis., and Timmonsville, S. C., and at all three stations they have displayed the relative alkaloid-producing tendencies evident in the original parent plant and the generation preceding.

While the plants at the different localities showed a parallel relationship toward each other, there was considerable difference in the general quantity of alkaloids produced. Thus, in the case of Madison and Arlington, where two pickings were made at fairly corresponding stages of growth, it was found that the Madison plants yielded more alkaloids than those at Arlington. At Timmonsville the yield was still greater than at Madison, but here only one picking was made, and it is hardly possible to make a true comparison. Nothing definite developed to indicate that a relationship exists between the amount of precipitation and sunshine and the percentage of alkaloids produced.

Plants were grown from cuttings, and at two stages of their growth these plants showed a marked tendency to display the same characteristic regarding alkaloid production as the plants from which they were propagated and the original parents of those plants.

Previous to the war Russian requirements in fertilizers were covered by foreign products imported to the amount of 612,000 short tons and fertilizers of domestic production to the amount of 252,000 short tons. The Ministry of Agriculture has started a thorough investigation of the deposits of phosphorite in Russia, which will be completed in about two years. There is said to have been investigated so far a supply of 2 tons of phosphorite. The quality of these deposits is far from satisfactory; only 8 per cent of the investigated supply contained more than 24 per cent of phosphoric acid, while the rest represented no industrial value. The deposits on the upper course of the Kama River, containing 27 to 28 per cent of phosphoric acid, are worthy of consideration for both quality and quantity, as well as the fact that they are situated near the deposits of sulphurous iron pyrites in the Ural Mountains.

DIFFERENCE IN WEIGHT BETWEEN RAW AND CLEAN WOOLS.*

By WALTER S. LEWIS.

This investigation was made (1) to obtain some definite knowledge as to the shrinkage of some of the foreign raw wools imported into this country, (2) to ascertain the shrinkage variation in two samplings of the same fleece, and (3) the difference in shrinkage between two fleeces of the same breed of sheep which were grown in the same section of country. Raw wool may contain from 15 to 80 per cent of grease and dirt, according to the breed of the sheep from which it is shorn, the kind of food upon which the sheep has lived, character of the country with reference to grass, sand storms, climatic conditions, and many other causes. The knowledge of the shrinkage is an important factor in purchasing, as it affects the price to be paid and the quantity of clean wool to be expected after scouring.

The term "shrinkage," as used in this paper means the total loss, by weight, of all grease and dirt taken out when the wool is scoured.

The fleeces employed in this investigation were secured from the Departments of Agriculture of[1] South Australian and New Zealand through the courtesy of the Commercial Museum of Philadelphia.

Entire fleeces were not tested, but large handfuls of wool were selected from 10 different parts of each. The samples thus obtained were drawn from parts well distributed over the whole fleece (not including the skirts) and therefore gave the average. Then one-half of each handful was placed together as one sample and is designated as "A" and the remaining portion of the sample marked "B" and held for further reference.

The extraction of the grease was accomplished by scouring in warm water containing pure olive-oil soap, thoroughly washing out the soap, and then extracting the remnant grease with ether. The loss in weight of the original raw wool by these processes is therefore called the shrinkage and the pure wool fiber remains.

All determinations of weight, both upon the raw and thoroughly cleaned samples of wool were made in an atmosphere of 65 per cent relative humidity at 70° F temperature.

The usual method of determining shrinkage is for expert buyers to estimate by the appearance and the feeling. In commercial scouring there remains between 1 and 3 per cent of the wool grease; therefore, to arrive at the shrinkage which would obtain in ordinary mill practice from 1 to 3 per cent must be subtracted from the shrinkage results shown in the tables of this paper.

1. The 49 fleeces herein described were carefully

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*The wool was selected by the School of Mines wool expert in the ordinary commercial way, is representative of the staple, and is in nowise to be regarded as an exhibit of the state's best wools, the fleeces being taken from bulk and packed without any further handling.

sampled and thoroughly cleansed of all grease and dirt, the results showing shrinkages from 19.5 to 54 per cent, according to the breed of sheep.

2. In the South Australian wools the greatest shrinkage difference between two determinations upon samples drawn in the same manner from the same fleece was 3 per cent, while for the New Zealand wools the largest difference was 6 per cent. These differences were calculated on the basis of raw-wool weight. This percentage variation within individual fleeces seems large, especially when the sampling was performed as described in the beginning of this article. If a sample had been drawn from one part of the fleece and another had been drawn from an entirely different place, greater percentage variations would undoubtedly have occurred.

TABLE I.—WEIGHT OF FLEECE, SHRINKAGE, AND PERCENTAGE OF DIFFERENCE BETWEEN THE TWO SAMPLES A AND B SELECTED FROM THE SAME FLEECE.

SOUTH AUSTRALIAN WOOLS.

Class of sheep.	Weight of fleece. Pounds.	Percentage shrinkage. Sample A.	Sample B.	Difference	Percentage shrinkage of fleece
Lincoln merino come back	8.0	45	45	0	45
Lincoln merino half-bred	11.4	46	44	2	45
Leicester merino half-bred	6.4	40	40	0	40
Medium merino	8.4	40	40	0	40
Strong merino	10.6	38	39	1	38.5
Lincoln merino half-bred	7.8	38	38	0	38
Leicester merino half-bred	7.3	37	37	0	37
Fine merino	6.8	36	36	0	36
Medium merino	6.0	34	36	2	35
Lincoln merino come back	5.1	33	34	1	33.5
Strong merino	6.3	33	33	0	33
Fine merino	5.3	33	33	0	33
Romney merino half-bred	5.8	31	31	0	31
Lincoln full-blood	12.1	30	30	0	30
Romney marsh pure	8.1	27	28	1	27.5
Leicester full-blood	9.8	28	27	1	27.5
Romney merino half-bred	5.5	26	27	1	26.5
Leicester full-blood	11.6	26	26	0	26
Romney marsh (pure)	7.1	23	22	1	22.5
Lincoln full-blood	18.3	19	22	3	19.5
Merino ewe 64's	9.6	53	55	2	54
Strong combing merino ewe 60's	9.6	51	51	0	51
Strong combing merino ewe 60's	8.7	51	49	2	50
Half-bred hogget 50's	11.8	49	48	1	48.5
Fine combing merino ewe 64's	8.7	48	47	1	47.5
Fine combing merino ewe 64's	8.4	46	46	0	46
Romney hogget ewe 44's	13.1	47	43	4	45
Corriedale ewe 50's	11.9	39	39	0	39
Three-quarter bred hogget 46's	*5.6	37	37	0	37
Lincoln ewe 48's	15.0	36	31	0	35
Half-bred ewe hogget deep 56's	8.2	34	35	1	34.5
Three-quarter bred hogget	6.3	35	33	2	34
Romney ewe 46's	7.5	32	34	2	33
Half-bred ewe 50's	*12.1	32	32	0	32
Romney hogget 46's	12.1	28	33	5	30.5
Cross-bred ewe 40's	10.0	29	31	2	30
Corriedale hogget 50's	13.6	33	27	6	30
Romney ewe 44's	16.1	28	28	0	28
Half-bred hogget 56's	*10.5	28	28	0	28
Cross-bred hogget 46's	*8.0	31	25	6	28
Cross-bred Romney Lincoln ewe 48's	7.0	27	28	1	27.5
Cross-bred Romney Lincoln lamb medium 46's	2.2	28	26	2	27
Romney ewe 46's	12.1	25	26	1	25.5
Cross-bred ewe 46's	5.1	24	24	0	24
Cross-bred hogget 44's	*10.0	24	24	0	24
Cross-bred Romney Lincoln lamb (strong) 40's	2.0	21	22	1	21.5
Half-bred ewe 50's	5.7	22	20	2	21
Cross-bred Romney Lincoln lamb (fine) 48's	1.9	20	21	1	20.5
Lincoln ewe 36's	15.7	21	18	3	19.5

Note.—The figures marked with an asterisk (*) denote fleeces which were skirted.

3. The difference in shrinkage between two fleeces of the same breed of sheep grown in the same location was found to be as great as 9.5 per cent. The results of such tests upon 13 different breeds of sheep showed a mean variation of 4.5 per cent in the shrinkage.

The data in Table II are given to show that two fleeces of the same breed of sheep may have a marked difference in shrinkage. This difference in the random samples recorded in the table reached as high as 9.5 per cent. Each fleece was in good condition, was not selected to give wide variations of shrinkage, but simply chosen at random to ascertain whether appreciable differences occurred.

TABLE II.—VARIATIONS IN SHRINKAGE IN THE SAME BREED OF SHEEP.

Table of Shrinkages of Two Fleeces Each of 13 Breeds of Sheep Showing that Fleeces Selected at Random May Exhibit a Wide Variation in Shrinkage Even in the Same Breed.

Class of sheep.	Percentage shrinkage. First fleece.	Second fleece	Difference.	Average shrinkage of both fleeces. Per cent.
Strong combing merino ewe	51	50	1.0	50.50
Fine combing merino ewe	47.5	46	1.5	46.75
Lincoln merino half-bred	45	38	7.0	41.50
Leicester merino half-bred	40	37	3.0	38.50
Medium merino	40	35	5.0	37.50
Strong merino	38.5	33	5.5	35.75
Fine merino	36	33	3.0	34.50
Cross-bred Romney Lincoln ewe	35	27.5	7.5	31.25
Romney merino half-bred	31	26.5	4.5	28.75
Romney ewe	31	25.5	6.5	28.25
Leicester full-blood	27.5	26	1.5	26.75
Lincoln full-blood	30	20.5	9.5	25.25
Romney marsh (pure)	27.5	22.5	5.0	25.00

The Secretary of Commerce announced on Oct. 13 that 50 tons of coal-tar dyes consigned to him for the account of William A. Mitchell of Lowell, Mass., representing the National Association of Cotton Manufacturers, were arriving on the steamship St. Louis, due this date. Several months ago the Secretary consented to act as consignee of two cargoes of dyes from Germany, for which safe passage was assured by permits granted by the British Government upon the express condition that the Secretary of Commerce would be the consignee. Arrangements were made by American manufacturers with the British Government whereby that government has permitted the exportation to the United States of the dyes coming on the St. Louis. It is hoped that this is the first of a series of similar shipments. The Secretary of Commerce has expressed his willingness to act as official consignee of merchandise coming from any foreign country whose authorities may deem such a course necessary.

THE PLANT

ELECTRIC STEEL COSTS.*

By F. T. SNYDER.†

It is now widely known that steel of high quality can be made electrically. It is known to a considerable number of metallurgists that properly designed electric furnaces will operate reliably and regularly with a lower percentage of lost time than a fuel furnace of equal output. It is convincingly known to only comparatively few makers of steel that electric steel can be made at a cost substantially below the corresponding cost with fuel furnaces. These few naturally include the operators of the furnaces that are making such records.

To render this information more widely available, this paper gives the operating costs for two sizes of furnaces in common use and of a type designed by the writer. In each case the costs represent records extending over continuous commercial use for periods of from one and a half to two years. As these costs are markedly lower than records of similar character of earlier types of electric steel furnaces, some of the reasons are given why such lower records should be expected with this latter furnace design.

This style of furnace from which these operating costs were obtained, is shown by the diagram. (Fig. 1.)

The furnace consists of a circular shell lined with refractories. The current enters at A at the bottom of the crane and passes into the furnace by a single electrode E in the center of the furnace. The heat is generated in the arc by which the current jumps from the electrode to the slag covering the metal. The electric current leaves the furnace at C through a contact with the metal bath.

These operating costs as given do not include supervision, as the amount involved is so small, due to the simplicity and reliability of these particular furnaces, that no additional cost to the plants containing these furnaces resulted on account of such supervision.

No overhead, due to cost and maintenance of buildings, is included in these costs, as the intention is to make these records of use to prospective users of such electric melting furnaces, and the building overhead cost varies widely from plant to plant, and is substantially independent of the sort of furnace used. The metal loss, due to spills and oxidation, is not included, as these depend largely on the care used by the melter. In each of the furnaces from which these costs come, the metal loss has been substantially below 1 per cent of metallic contents of the charge. The cost for scrap used are real prices over long periods of time for special scrap material, and are due to the ability of these electric furnaces to handle low-priced material.

In comparing these operating costs with other published records, it should be kept in mind that these costs do not represent single heats, or runs made under test conditions, or under exceptional circumstances. These costs are the average of regular commercial operation during long continued industrial service.

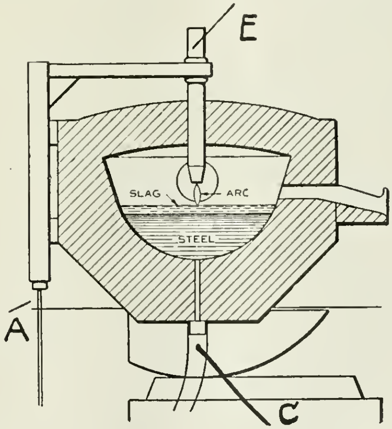

Fig. 1. One Electrode Type Steel Furnace.

These costs include the stand-by losses between heats, the breakages and waste of supplies, the lost time on Sundays and holidays, the overtime work on maintenance.

ELECTRIC STEEL MELTING.

COSTS OF OPERATION WHEN MELTING COLD SCRAP AT 10-TON OUTPUT.

		Per day.	Per ton.
Output:			
Heats in 11 hours		4	
Tons of metal in 11 hours		10	
Labor:			
Melter	$4.00		
Helpers	2.50		
		$6.50	$0.65
Electricity (per kilowatt hour 0.7c.):			
Furnace	$34.70		
Substation	4.00		
		38.70	3.87
Supplies:			
Refractories	$3.00		
Electrodes	6.00		
		9.00	.90

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*A paper presented at the 28th General Meeting of the American Electrochemical Society, in San Francisco, September 16-18, 1915.

†Snyder Electric Furnace Co., Chicago.

Maintenance:			
		2.40	.24
Direct cost		$56.60	$5.66
Burden:			
Interest, depreciation and taxes.		18.00	1.80
Conversion cost		$74.60	$7.46
Charge:			
Scrap	$110.00		
Alloys	6.00		
		116.00	11.60
Total cost melted metal		$190.60	$19.06

COST OF ELECTRIC STEEL.

COSTS OF OPERATION WHEN MELTING COLD SCRAP AT 6-TON OUTPUT.

		Per day.	Per ton.
Output:			
Heats in 12 hours		4	
Tons of metal in 11 hours		6	
Labor:			
Melter	$3.00		
Helpers	1.40		
		$4.40	$0.74
Electricity (per kilowatt hour 1.4c.):			
Furnace	$45.02		
Substation	1.84		
		46.86	7.81
Supplies:			
Refractories	$1.70		
Electrodes	3.00		
		4.70	0.78
Maintenance:			
		.84	0.14
Direct cost		$56.80	$9.47
Burden:			
Interest, depreciation and taxes		11.30	1.88
Conversion cost		$68.10	$11.35
Charge:			
Scrap	$58.00		
Alloys	2.04		
		60.04	10.01
Total cost melted metal		$128.14	$21.36

While these costs are taken directly from long continued industrial operations, they are so low compared with similar records for furnaces of earlier design, that they naturally do not carry immediate conviction to operators who have had direct access to similar records of such earlier furnaces. It is desirable to show in some detail why such low operating costs should be expected with this type of furnace.

Considering the cost items in the reverse order from that in which they appear on the cost statement, the item of burden, which includes interest, depreciation and taxes, is low due to the rapid melting ability of these furnaces. Each of these furnaces has regularly made four heats in an eleven-hour shift. This is about double the output for the size of furnace of that from furnaces of earlier design, and the burden item per ton of output is therefore correspondingly reduced.

The item of supplies is made up of electrodes and refractories. Each of these furnaces runs regularly on less than four pounds of electrode per ton of steel poured, as compared with an average of 30 pounds for furnaces of earlier design. This large difference is due to the joint operation of several causes. The most important of these is the use of a single electrode in place of three electrodes. Electrode consumption is largely a matter of surface burning. Three electrodes of the same size would naturally burn three times as much as a single electrode. Actually, the ratio is much higher than three to one for the following reasons:

The highest permissible voltage that can be used is determined by considerations of safety to furnace operator. With a three-electrode furnace the voltage between electrodes is 173 per cent of the voltage from each electrode to the bath. Due to the extra heat losses with a three-electrode furnace the total energy to be introduced through the electrodes for the same tonnage output per day is about 150 per cent of the energy required with these single-electrode furnaces. This lower arc voltage and consequent larger current to be carried, and the large input, result in three electrodes for the three-electrode furnaces each as large as the single electrode of these one-electrode furnaces, if made of the same material. Electrode cost is made up of two items: The heat lost through the electrode during its life and the original cost of the electrode. In commercial operation in this country cost conditions are such that the higher consumption with the three electrodes makes the first cost the prime consideration. It is more economical with three electrodes to use amorphous carbon, and more economical with a single electrode to use graphite. Amorphous carbon has a lower current carrying capacity than graphite and this, with the lower voltage permissible with equal safety, results, with good engineering, in three electrodes each about twice the diameter of the single electrode; thus exposing six times the area of surface to burning with the same tonnage output. In addition amorphous carbon burns more readily than graphite, so that the actual ratio from practice of from eight or nine to one for the relative electrode consumption of a single and three-electrode furnace is what should be expected.

Most of the refractory wear in an electric furnace is on the roof. The sides are banked up with relatively cheap material that keeps the walls from wearing. This roof wear is largely around the electrodes and is partly due to the hot gases that escape between the electrode and the roof. With three electrodes this wear of the roof near the electrode would be expected to be three times as large with a three-electrode furnace as with a one-electrode furnace. It is further increased due to the fact that three-phase current is used with three electrodes. This gives a difference of potential between electrodes 73 per cent higher than the potential from each of the three electrodes to the bath. Fire-brick at steel melting temperature is a relatively good conductor of electricity, having a resistance of about one ohm per inch cube.[1] Consequently, a considerable current flows between electrodes through the hot roof material. This current flow further heats the roof just as the current heats the filament of an incandescent lamp, and heats it just at the places where the roof is already at the highest temperature. To reduce this leakage current between electrodes, the electrodes of a three-electrode furnace are moved as far apart as practical. The further they are moved apart the nearer the arcs come to the walls and the higher the cost of wall refractories per ton of product. With these single-electrode furnaces, the arc is at the center at the maximum distance from the walls, with consequent low wall wear.

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[1] Extension of curve of data given by A. Stansfield: Trans. Am. Electrochemical Soc., 22, 93 (1912).

With equal safety to operators, the arc voltage of a single-electrode furnace is substantially double that of the voltage of each arc of a three-electrode furnace. The length of an arc under steel melting conditions increases rapidly with increase of voltage. The temperature of an arc in a steel furnace is determined by the amount of energy it has to radiate per square inch, substantially according to Steffens' law. With these single-electrode furnaces the energy consumed is low, and the arc surface is large. Therefore the arc temperature is low.

The refractories are at a temperature between the arc temperature and the temperature of the bath, as in an arc furnace about 50 per cent of the energy reaches the bath by reflection from the lining of the furnace. Therefore, the lower arc temperature of these single-electrode furnaces means a lower refractory temperature. At steel melting temperatures even a few degrees' drop means a large extension of the life of the refractories, so that it should be expected that with these furnaces with low temperature arcs the refractory costs should be low.

The electric heat used in an electric steel melting furnace is made up of two parts. One part goes into the metal and goes with the metal into the ladle. This part is a fixed amount per ton for a definite pouring temperature. It is the same for all steel melting furnaces, both fuel and electric. The other part represents the heat lost during the melting operation. It all appears in the heated air around the furnace or in the cooling water from the various jackets used. This heat is lost through the doors, the roof, the shell and the electrodes.

These furnaces are fitted with a door in the form of a plug, so that in place of the usual 4½-inch (11.5 cm.) of door brick, they present the resistance of 14 inches (35 cm.) of thickness to the flow of heat. Thorough tests of the sliding type of door usually used with earlier furnaces show a door loss exceeding 100 kilowatt-hours per ton of steel. Much of this is saved by this plug type of door. We have no experimental results on the actual heat losses with the plug type of door, but our calculations, based on its outside temperature, show probable heat losses of 3.3 kw. per furnace door.

These furnaces have roofs substantially 50 per cent thicker than those of earlier design. Special attention has been given to the design of the shell linings of these furnaces, which are made up of a series of concentric refractories, each proportioned for its specific part of the heat insulation work. They are designed for and operate with external surface temperatures at about 60° C. It is practical to hold the hand against the outer surface of the shell of these furnaces. In actual practice the radiation losses are so low with these furnaces that no extra means are used to keep them hot between heats. With furnaces of older design it is usual to keep current on at reduced input, or to use an oil burner during the off-shift when a furnace operates only one shift a day. With these furnaces, which both operate eleven hours a day only, no electricity or oil is used on the off-shift. The furnaces are luted up after the last heat of a shift and when opened for the next day's operation have lost so little heat as to be ready for immediate operation.

The principal unavoidable heat loss in an electric furnace is through the electrodes. Just as a copper wire conducts electricity better than air, so a carbon electrode conducts heat much better than would the air in an empty electrode hole. With the three electrodes used with most furnaces of earlier design, and with the three electrodes of the same size as the single electrode, the heat loss would obviously be three times as great as in the single-electrode furnace. Actually, the ratio is much higher, due to the economic necessity of using amorphous carbon electrodes in three-electrode furnace. As used in the best actual practice the cross-sectional area to the three carbon electrodes of a three-electrode furnace is about fifteen times the cross-section of the one graphite electrode of the single-electrode furnace. Carbon at these temperatures has about half the heat conductivity of graphite,[2] so that the heat lost through the three electrodes is about seven and one-half times the heat lost through the one electrode. However, with the single-electrode furnace a contact is also required to connect the charge with the circuit. This contact loses some heat, hence the net result is that the heat loss due to the introduction of the current in a well designed three-electrode furnace is about five times the heat loss in a one-electrode furnace.

A substantial loss of heat with the older designs is due to furnace delays. If the pouring gang are not ready to take the heat the moment it is finished, the high radiation losses of the furnace of older design keep on and are frequently augmented by the melter allowing the temperature of the bath to keep on going up. The furnaces from which the records given here were taken are inherently designed to regulate automatically for maximum temperature. As the temperature reaches that for which the furnaces were designed, the electric input is just sufficient to keep up the radiation. This reduces largely the loss of heat due to furnace delays. In addition, it prevents largely the overheating of refractories. This regulation for maximum temperature is secured without auxiliary apparatus of any kind. In each case it is an inherent characteristic of the furnace design.

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[2] Carl Hering: Trans. Am. Inst. Electrical Engineers, March, 1910, p. 285, gives the conductivity of graphite at 1600° C. as 2.9 watts per inch cube, of amorphous carbon 1.5 watts.

The low labor cost with these furnaces is due primarily to the simplicity of the mechanical and electrical construction. The smaller of the furnaces is handled entirely by a single man, except when charging, when three helpers are used to shorten the charging time. Due to the fact that the furnace is entirely and inherently self-regulating, this single melter, for something over half his time, has nothing to do at the furnace. On accasions each of these furnaces has been left for an hour at a time without attendance, at work at full power. This extra time the single melter uses in making ready the next roof and in shearing up scrap for easy shoveling.

The other material factor in the low labor cost per ton of these furnaces is their rapid melting ability and the consequent relatively large tonnage output per man, as shown in the labor items in the tables given, expressed per ton of steel. This output capacity is in turn due to the fact that the electric input is not wasted, but very largely goes to melting steel. This effect is cumulative, as the shorter time of heats reduces the radiation time chargeable to each ton, and so releases further energy for melting steel. This in turn reduces the labor cost per ton of output for a definite size of furnace.

In closing, it may be stated that these furnaces show a thermal efficiency not far from double that usual with furnaces of older design. The most reliable figures we can get for regular operation of furnaces of older design operating on a single shift show about 1,000 k.w.h. per ton of steel, of which only 33 per cent goes into the ladle with the fluid steel and slag, our furnaces under equivalent conditions use only about 560 k.w.h. per ton of steel, the corresponding efficiency being 63 per cent. This is important commercially. The slow progress of electric steel making in the first ten years of its commercial existence was due to its high costs. It could not compete with most types of fuel furnaces in cost per ton of output. Its plea for existence had to be based on quality of product. The advance in this country, where quality was relatively unimportant, was slow. These furnaces of newer design give costs that are lower than most types of fuel furnaces. The higher quality of electric steel is secured for nothing. The real competition in the past has not been between different types of electric furnaces, but between all types of electric furnaces and fuel furnaces. Now that properly designed electric furnaces can compete in cost with fuel melting on steel their introduction in this country should be accelerated.

Mining of chrome iron ore is active at Black Lake, Quebec Province, Canada.

NEW APPARATUS FOR THE MANUFACTURE OF AQUA AMMONIA FROM RAW GAS LIQUOR.[*]

By R. W. HILGENSTOCK.[†]

Owing to the great demand on ammonia for the manufacture of nitric acid in this country, the manufacture of concentrated ammonia liquor and aqua ammonia has drawn considerable interest. While the manufacture of concentrated ammonia liquor is comparatively easy and only few apparatus are needed, the manufacture of aqua ammonia, if to be absolutely pure, is much more difficult. Carbonic acid, sulphuretted hydrogen and the empyreumatic compounds must be taken out entirely. By means of alkalis, carbonic acid and sulphuretted hydrogen may be bound, so that they will not be absorbed with the ammonia gases; but it is an expensive process, to say nothing of the unpleasant residues, specially when lime is used. The city authorities are always anxious to know how these residues are taken care of, and the sanitary offices often make trouble, because they fear contamination of the rivers and wells.

To avoid these troubles as much as possible, the utmost care had to be taken in design and manufacture of new apparatus. The question also rose whether the lime or other alkalis, used, could not be replaced by other materials. They have been found in the heat and the alkaline properties of the ammonia gas itself. Carbonic acid and sulphuretted hydrogen form compounds with the ammonia, that can be decomposed very easily by heat; and on the other hand, the ammonia very readily re-unites with carbonic acid and sulphuretted hydrogen.

These particular properties are the base of the apparatus described in the following pages which is built by the "Poetter G.m.b.H., of Düsseldorf, Germany."

The general arrangement of an aqua ammonia plant of the "Poetter type" is shown in Fig. 1. The raw liquor to be worked up, is pumped into the feed-tank, 1, which, at the same time, acts as a regulator for the equal flow of the liquor into the carbonic acid extractor. For pumping the liquor from the storage well to the feed-tank, it is advisable to provide a motor driven centrifugal pump, and by a valve or cock in the discharge line, it is easy to regulate the flow of liquor to the tank.

In the carbonic extractor, 2, the greatest part of the carbonic acid is contained in the gas liquor in the form of carbonate of ammonia, which has to be taken out. This takes place in the lower part of the apparatus, and for this purpose there are three rectangular heating chambers, in which the gas liquor is heated to 98-100° Cels. The proper decomposition temperature is in the neighborhood of 93°, so this temperature is sufficient for the lowest heating chamber, but in order to decompose almost all the carbonate of ammonia, and thereby extract the major part of carbonic acid, it is necessary to keep the temperature nearly 100° Cels.

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[*] From The American Gas Light Journal.

[†] Chief Engineer, Poetter G. m. b.H., Düsseldorf (Germany).

At this high temperature, of course, a great deal of the ammonia is driven off also, and in order to regain it and prevent losses, a number of absorption chambers are placed on top of the upper heating chamber, in which the ammonia is reabsorbed from the liquor, which again flows into the heating chambers. The absorption of the ammonia is absolutely perfect, so that the waste gases that leave the apparatus contain only air, carbonic acid, sulphuretted hydrogen and pyridin. To prevent the formation of vacuum in the apparatus, a vacuum breaker, 3, is attached, which admits air from the outside if minus pressure is produced.

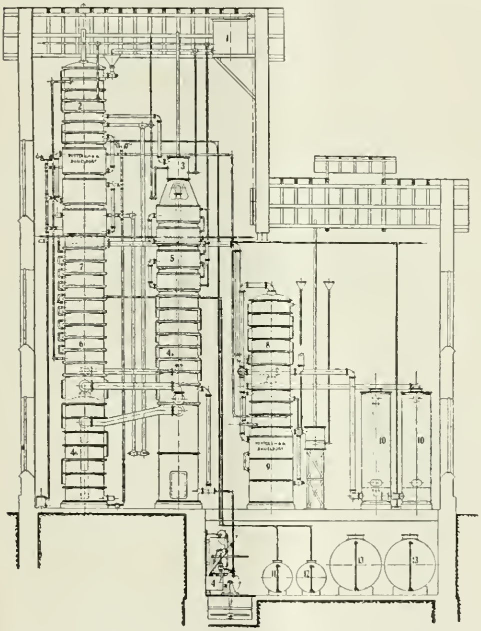

Fig. 1. General Arrangement of Aqua Ammonia Plant.

From the lower heating chamber, the preheated and decarbonized liquor flows into the upper section of the still, 4a, in the upper sections of which all volatile ammonia compounds, and the last carbonic acid and sulphuretted hydrogen are eliminated. In the liming leg, which is below the sections for volatile ammonia, the liquor is thoroughly mixed with milk of lime, pumped from the lime mixing vessel, 4; the lime causes the decomposition of the so called "fixed" ammonia—salts, i. e., sulphate of ammonia, salammoniac, nitrate of ammonia, etc. In order to drive off the ammonia, set free by this reaction, the mixture of liquor and milk of lime is led into the secondary still, 4b, composed of several sections, similar to those of the primary still. The steam-ammonia vapor pass the primary still with the vapors set free in this part of the apparatus, and enter the condenser, 5, on top of the primary still; and, due to the special construction of this apparatus, which consists also of several individual chambers, the ammonia gases are almost entirely freed from the steam vapors, so that a nearly dry ammonia gas enters water washer, 6.

In this washer the remaining carbonic acid and sulphuretted hydrogen in the ammonia gases are to be extracted; a number of sections, similar to those of the still, being provided for this purpose. In each section the ammonia vapors are distributed over a large washing surface, causing a thorough washing of the gases. The washing fluid is clear water, which enters the upper section and travels down from section to section. A certain part of the ammonia is absorbed by the water, so that a saturated solution of aqua-ammonia is formed. The ammonia in this solution retains the last parts of carbonic acid and the sulphuretted hydrogen, forming carbonate and sulphate of ammonia, respectively. The gases leaving the washer contain, if any, only traces of CO_2 and H_2S. The feed of the washing water is regulated, so that just enough water enters the washer to absorb sufficient ammonia to retain the carbonic acid and sulphuretted hydrogen. It is, therefore, only necessary to test the ammonia gases, from time to time, at the outlet of the washer, with a solution of calcium chloride and a solution of acetate of lead; in the first solution no precipitation must show, and the latter solution must not discolor when brought in contact with the ammonia gases.

The waste-wash water, a saturated solution of carbonate and sulphide of ammonia, is led into one of the cylindrical tanks, 11 or 12, from where it is forced in thin streams by means of compressed air, into the carbonic acid extractor, where a decomposition of the volatile ammonia compounds takes place again, carbonic acid and sulphuretted hydrogen are eliminated, while the ammonia is absorbed by the gas liquor. To prevent any CO_2 and H_2S being retained in the ammonia, in case trouble occurs in the operation of the appartus, another washer, 7, is placed above the water washer. Its construction is exactly the same as that of the water washer, but instead of water, a 15° Bé. solution of hydrate of sodium is used as washing fluid, and any CO_2 and H_2S contained in the ammonia gas are taken up by the sodium solution, forming carbonate of soda and sodium sulphide. The waste washing fluid from the lower section of this washer is led to the storage liquor-well, as only small quantities are produced.

The ammonia gas so far purified, still contains some tarry matters and some pyridin that must be taken out. For this purpose an oil washer, 8, is provided, similar in its construction to the other washer. It consists of a certain number of sections in which the ammonia gases come into intimate contact with the washing fluid, in this case a heavy tar oil. After this third washing the ammonia is sufficiently pure; so it can be absorbed in distilled water in the absorbing apparatus, when so-called "technical aqua ammonia" is to be manufactured.

This absorbing apparatus, 9, is the same in construction as the carbonic acid extractor, 2. Instead of steam, cooling water is used in the 3 rectangular chambers, to prevent a rise of temperature in the absorbing water, due to the reaction heat. According to the quantity of distilled water fed into the upper part of the apparatus, aqua ammonia, higher or lower in the percentage of ammonia, is the end product. The advantage of this apparatus is that the finished aqua ammonia flows out continuously, a changing of the absorbing vessels, as is the case with other apparatus, is therefore not necessary. The distilled water for the absorbtion, is removed from the heating chambers of the carbonic acid extractor, the condensed steam being led through a cooler and into a storage tank. A steam trap is placed in the exhaust line from the coils in the chamber, so that only condensation, and no live steam, can get out.

When chemically pure aqua ammonia is to be manufactured, a further purification of the ammonia gas is necessary, which purification takes place in the charcoal and bone black filters, 10. Four wrought iron filters are installed, two filled with charcoal, and two with bone-black, and the gas passes the charcoal filters first, and then those filled with bone-black. The charcoal, as well as the bone-black, can be regenerated several times before they are used up. Before each regeneration, the ammonia retained in the filter material must be driven off by steam, and led back into the lower cylindrical section of the carbonic acid extractor, in which it is absorbed again by the raw ammonia liquor.

I give a table showing the operating costs and profits of a large aqua ammonia plant.

OPERATING COSTS AND PROFIT FOR AN AQUA AMMONIA PLANT WORKING UP 100 CBM., OF GAS LIQUOR, CONTAINING ABOUT 2% AMMONIA, PER 24 HOURS.

A. Expenses.

1. a. Interest and amortization for the building, i.e., 5% for interest and 3% for amortization—total, 8% of M. 40,000...............	M. 3,200
b. For the apparatus—5% for interest and 10% for amortization—15% of M. 60,000...	M. 9,000
2. *Costs for Steam.*—For each cubicmeter of gas liquor worked up 275 kg. are needed; the yearly amount of steam would be, $275 \times 100 \times 300 = 8{,}250{,}000$ kg. Figuring that 1 kg. coal will evaporate 7 kg. of water, there would be needed $8{,}250{,}000 : 7 = 1{,}200$ tons. The price of one ton is M. 20—consequently an expense of $1{,}200 \times 20 =$	M. 24,000
3. *Lime Consumption.*—For each kg. ammonia in the gas liquor, 0.7 kg. of good lime is needed. Figuring 20 kg. ammonia in 1 cbm. of gas liquor, the total amount of ammonia would be $20 \times 100 \times 300 = 600{,}000$ kg.; this would mean a lime consumption of $60{,}000 \times 0.7 = 42{,}000$ kg. The selling price of lime being M. 1.70 for each 100 kg., we had to consider $42{,}000/100 \times 1.70$..	M. 7,140
4. *Cooling Water.*—For each cbm. of gas liquor 2 cbm. of cooling water are needed. In 300 working days the total amount would be $100 \times 2 \times 300 \times 60{,}000$ cbm.; the cbm. will cost about 0.05 Mk., consequently an expense of $60{,}000 \times 0.05$	M. 3,000
5. *Consumption of Alkali (Sodium Hydrate).*—When sodium hydrate of 70% is used, it can be assumed that each kg. of ammonia in the gas liquor requires from 10 to 15 gramms of sodium hydrate, averaging 12.5 gramms. 600,000 kg. ammonia are worked up, so $600{,}000 \times 12.5 = 7{,}500$ kg. are necessary. 100 kg. of the material cost about M. 20—amounting to a total of $7{,}500/100 \times 20$	M. 1,500
6. *Oil—Consumption.*—Actual operating figures show the consumption of oil is about 0.01 to 0.02 kg. oil for each kg. of ammonia, an average of 0.015 kg. The total consumption, therefore, would be $600{,}000 \times 0.015 = 9{,}000$ kg. The price of oil being M. 35 for each 100 kg., the expenditure would be $9{,}000/100 \times 35$	M. 3,150
7. *Charcoal and Bone—Black.*—The consumption of these materials depends upon the composition of the gas liquor, and the impurities that must be taken out. The expenses, however, should be covered with 0.5 Pfg. for each kg. of ammonia, so that we had to figure with $600{,}000 \times 0.05$......	M. 3,000
8. *Wages.*—To operate the apparatus, wheeling the lime and preparing the milk of lime, 6 men are needed for 24 hours; two of these are operators, each with M. 6, and 4 helpers with M. 5 each; the yearly wages would, therefore, amount to 32×300....	M. 9,600
9. *Miscellaneous.*—For repair work, packing, cleaning, oil and other material, light and cleaning, costs can be figured............	M. 1,200
10. *Raw Gas Liquor.*—For each kg. of ammonia contained in the gas liquor, M. 0.60 can be figured, so that the total expenditure would amount to $600{,}000 \times 0.60$...........	M. 360,000
11. *Losses.*—For unavoidable losses 3% of the amount in item 10 has to be considered..	M. 10,800
Total	M. 435,590

RECEIPTS.

The selling price of the kg. ammonia contained in the aqua-ammonia is M. 0.90, so that the total receipts would be 600,000 x 0.90 ....M. 540,000

RECAPITULATION.

Receipts	540,000 Mk.
Expenses	435,590 Mk.
Net earnings	104,410 Mk.

The price for the raw ammonia liquor in item 10 is f. o. b. work, so that eventual freight charges had to be added.

It had to be considered also if it would not be of advantage to buy the liquor in concentrated form, with about 20 per cent of ammonia; in this case the kg. of ammonia would cost M. 0.80 f. o. b. works.

When "technically pure ammonia" is to be manufactured the expenses in item 7, amounting to M. 3.000, can be omitted.

Agriculturists of Yuba County, California, are beginning to experiment quite extensively with the culture of silk, acting on advice received from experts that it can be made a success in this part of the state. It is said the climate here is particularly well adapted to the growth of the mulberry tree and the development of the silkworm. The mulberry tree has been grown extensively throughout this section for many years and it has made possible the present experiments. In the past the industry has not been developed here because few understood the method by which it is conducted.

COLOR MANUFACTURE IN THE UNITED STATES.*

By J. F. SCHOELLKOPF†

Of all the industrially prominent countries the United States is doubtless the one which has been most successful in the manufacture of products of universal use. For articles of this class the large home market, cheap transportation and great consuming capacity of the American people, permits the construction of manufacturing plants on an enormous scale, where machinery takes the place of hand labor, so that in spite of high wages, the actual labor cost of such articles is frequently less than the labor cost on the same articles when produced in countries with a more limited consumption.

I call attention to the fact that at the last revision of the tariff, the steel corporation stated that they had no objection to a lowering of the duty on their products; the automobile industry, which manufactures on a scale unheard of in any other country, even before the present war was exporting its product to every corner of the globe; other articles in point are agricultural machinery, sewing machines, typewriters, leather, boots and shoes, and to mention a few chemical products, wood alcohol, acetate of lime, caustic soda, etc.

Unfortunately, the manufacture of synthetic dyestuffs does not lend itself to such mass production. The estimated annual consumption of aniline colors in the United States is about 40,000,000 pounds, of an approximate sales value of $15,000,000. While this amount is quite large when considered by itself, it is small when compared with the products enumerated above and from the manufacturer's viewpoint dwindles to small proportions indeed. I refer to the fact that while the producer of caustic soda manufacturers but one article, the aniline color manufacturer produces many.

The single process for making coal tar dyes has not yet been invented and never will be, nor can this industry get along with a single raw material as was suggested in a recent press report from Chicago, which explained the shortage of dyestuffs by the fact that Germany, being unable to obtain any more blood from the Chicago packing houses, was thus deprived of her most needed raw material for synthetic dyestuffs.

According to Schultz's Tables, 1914 edition, there were on the market at that time no fewer than 930 synthetic dyestuffs, being chemical individuals, not mixtures, or 1,000 in round figures, as there are a number whose constitution the color factories refuse to divulge. Of these, there are no two colors whose process of manufacture is exactly the same. There is as much difference in the manufacturing process of sulphur black and direct black, though both are used for similar purposes, as there is perhaps in making soap and woodpulp. And the same applies to auramine, methylene blue, fushsine, alizarine, nigrosine, chrome black, lithol red and others. Going back to the possible annual production in America of 40,000,000 lbs., and assuming that the trade demands all of the 1,000 products now on the market, this would necessitate, so to speak, 1,000 individual miniature factories, each having a capacity of about 40,000 lbs. This, of course, would not actually be the case, for among all colors used, there are about a dozen or so which constitute about 75 per cent of this country's consumption, including such colors as sulphur black, direct black, acid black, chrome black, nigrosine, indigo, auramine, benzo-purpurin, patent blue, paper blue, alizarine, fuchsine and phosphine. Assuming this to be approximately correct, that would leave 10,000,000 lbs. for the remaining 988 dyestuffs, or an average of about 10,000 lbs. for every little factory.

It is obvious that to produce so small a quantity the manufacturer could not run his factory the whole year round, and he is compelled, therefore, to rotate, that is, he must manufacture a number of different colors in the same installation in succession, each change necessitating extra labor in clearing the apparatus, and requiring more or less alterations to same. The monster European factories, having a very much larger production, do not suffer from this disadvantage to nearly the same extent.

Their larger output of individual colors is also an advantage in other respects. According to their latest report, the Farbwerke Hoechst, Germany, had in their employ more than 300 scientifically trained chemists. Allowing 100 of that number for their inorganic, analytical and research work, that would leave 200 to look after the manufacture of about 500 colors, as the concern named probably does not make more than 500 of the dyestuffs mentioned in Schultz's Tables. One chemist, therefore, has on the average no more than two or three colors in his direct charge, and this continuously during the whole year.

Every chemist who has had actual manufacturing experience will realize that only by being in daily contact with the product of his manufacture can he attain that efficiency which enables him to detect at once the slightest inaccuracy in his processes, and to turn out a product always uniform in quality and yield. On the other hand, when called upon to change from one product to another every few months, as is the rule in American color factories, slight details in the processes may have escaped his mind or other conditions may have changed, causing loss in yield and increasing generally the cost of production.

Corresponding to the variety of processes, that are carried out in a dyestuff factory, a great variety as well as a great quantity of chemicals, inorganic as well as organic, are used. Almost all of these, with the possible exception of high per cent anhydrous sulphuric acid, can be obtained in this country in normal times in sufficient quantities and at fair prices.

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*From an address delivered Oct. 22 before the Society of Chemical Industry.

†Of the Schoellkopf Aniline and Chemical Works, Inc., Buffalo, N. Y.

A very important part in our industry is played by the so called "intermediate" products, which have lately been mentioned so often in the daily press, and on which subject I. F. Stone has delivered a very able address on the occasion of the National Exposition of Chemical Industries. Most of these "intermediates" have been imported from Europe, principally Germany, and I confess that at recent tariff revisions I have sought to have these placed on the free list. This has, doubtless, created the impression in some quarters that the manufacture of these products was particularly complicated, difficult and practically impossible to produce. Nothing, however, is farther from the truth. Many of our most important intermediates—I will mention nitrobenzol, aniline, alphanaphthylamine, betanaphthylamine, betanaphthol, metanilic acid, sulphanilic acid, naphthionic acid, benzidine—are made by simple processes. You all know that benzol on nitration with so-called mixed, that is, nitric-sulphuric, acid yields nitrobenzol, and washing and distilling the product will yield practically chemically pure material; on reduction with iron aniline oil is formed and purified by simple distillation.

Very similar to this is the process of making alphanaphthylamine, substituting naphthaline for benzol. Betanaphthol, which is used also in great quantities for the so-called "Parared," is made by sulphonating naphthaline to the so-called betamonosulpho acid; this is isolated, melted with caustic soda, and the betanaphthol then separated with acid and on distillation yields again a practically c.p. product. In fact, before the war, and while these intermediates were on the free list, we have found it cheaper to manufacture several of them in our own works rather than import them, duty free, from abroad. However, in other cases, some of these coal tar derivatives consume such large quantities of chemicals, i. e., mostly mineral acids, which in part cannot be obtained at all, or partly at a materially higher price than in Germany, and furthermore, the yield is comparatively small, or, in other words, the amount of labor to produce a pound is so much greater that we could not compete with the German factories and had to import those materials.

Even the large German factories, it is safe to say, do not manufacture all of their own intermediates; some of them constitute only a very small part of a given dyestuff, and I am sure can only be made successfully by factories that specialize in them, and do not entirely depend on their own consumption.

As I mentioned before, the process of making dyestuffs is in no two cases exactly the same. This is the cause of a large variety of complicated machinery, as is, in my belief, not used in any other industry.

Another peculiar feature of the dyestuff industry is the fact that it is subject, to a great extent, to the change in style, more so if it depends only on the home market. While, say, an iron furnace to take care of an increased demand, need only add more units of the same kind, a color factory is, even in normal times, confronted with the falling off of sales of certain shades, while others enjoy a particular boom, necessitating a constant shifting of manufacturing and a correspondingly great, let me say, flexibility of apparatus.

From the aforesaid it will be seen what an important position falls to the engineering force of a color factory. The Badische factory in Ludwigshafen alone is said to employ over two hundred engineers with college training.

Altogether, you will have seen that the manufacture of synthetic dyestuffs is a very intricate one, at the same time highly interesting, not only from the chemical, but also from the engineering viewpoint.

It is deplorable that, as I mentioned already, so many reports have been published in the papers, which only tend to mislead the public, and worse yet, the government, about the problems which confront the American manufacturer of dyestuffs.

We must not forget that Germany, of course, is by far in the lead, and there are quite a few colors which the German manufacturer has patented in this country which, consequently, are beyond competition, but the inventions in this line, of the last few years, have had by no means the revolutionizing effect of the older inventions like the Hoeschester ponceaus, which replaced cochineal; of alizarine, which replaced madder; of indigo, which put the natural product out of business; or if acid and direct blacks, which compete successfully with logwood. In spite of these latest inventions, however, the consumption of the older colors seems to increase steadily. I also doubt that there is any great invention to be expected which would interfere materially with the older colors. This does not mean that research in the line of finding new products should be abandoned altogether.

With due co-operation between university and industry, as has been the case in Germany for many years and to which is due, to a large degree, the greatness of the German dyestuff industry, there are many promising problems yet to be solved, but just as much, or perhaps more, has been accomplished by working in the older field, in consequence of which our industry has been able to lower their prices from year to year in contrast with almost all other industries, which, in proportion to the rise in wages, have had to raise their prices if they did not choose to lower the standard of their goods instead.

Gentlemen, viewed from a manufacturer's standpoint, the present condition of the aniline color industry in America is a most trying one, owing to the difficulty in securing adequate supplies of all kinds and even the ordinary heavy chemicals, such as sulphuric and nitric acids.

In closing, I would like to summarize the needs of the industry after we return to normal conditions. We will require:

(1) A plentiful supply of chemicals, including the so-called heavy chemicals. All of these will, doubtless, be obtainable from American sources;

(2) All basic raw materials derived from coal tar in practically pure form, such as benzol, toluol, xylol, naphthaline, anthracene, carbazol, and carbolic acid. Some of them are obtainable now, in fact the war has greatly stimulated the manufacture of a number of these products, unfortunately mostly for use in explosives. But, as the manufacturers are reaping enormous profits on these products during the war, they will be able to write off their plants, and after the war should be in a position to furnish an ample supply of these chemicals for color purposes.

(3) We need intermediates. Very few of these are made at the present time in this country for reasons I have outlined before. But even the many that are missing present no serious problem from the manufacturer's viewpoint, always keeping in mind that there must be found a way to offset the higher manufacturing costs. In frequent conferences with large chemical concerns intending to take up the manufacture of intermediates, we usually found no willingness to enter into their manufacture if we could not guarantee to take, say, upwards of fifty tons or so annually of each product.

(4) We need the co-operation of the American consumers, which, I regret to say, was extended to us in the past only to a very limited extent. I believe, however, the war has taught them a lesson, which the present generation will hardly forget.

(5) And, most important of all, we need legislation which will help to create the industry by first creating conditions that will make it profitable, as every manufacturer is entitled to a reasonable return on his investment.

If these conditions are fulfilled, I venture to say that American mills will soon be using American aniline colors, and any possible slight increase in cost will be more than offset by the assurance that they will be protected absolutely against any future recurrence of the present calamitous situation.

PRIMITIVE OLIVE-OIL MANUFACTURE IN PALESTINE.*

All olive oil made in the Jerusalem consular district, whether by the older processes or by more modern machinery, is considered as edible without refining, with the sole exception of that last pressed from the bruised berries. This, being dark and containing much of the pulp, is fit only for the soap industry, and then only after being mixed with better qualities.

The old native oil presses consist of a circular stone trough elevated a little from the ground, in which a stone disk rotates around an upright shaft. This disk turns on its edge like a wheel and is operated by a horse, mule or camel. One man is constantly stirring, removing, and replacing the olives as they are crushed, another man carrying the whole olives to the mill and returning with the crushed ones. Once sufficiently crushed they are placed where they can be filled into circular baskets that have a small opening and are quite flat. These baskets have been in use for a long time.

The older extraction method, and one still much in use, calls for a wooden box for a mould, in which a large piece of coarse goat's-hair cloth is laid. The box is filled with the crushed berries, pressed compactly together, after which the cloth is folded over the top in a cater-cornered style. These are now ready for the press. This method of crushing the olives is the oldest known, possibly dating back hundreds of years, as ruins of mills would seem to indicate.

Modern mills using imported machinery, when without power, employ exactly such a crusher; when driven by a motor, as many now are, two smaller stone disks are used, both placed on the same axle. In all cases these stones are from the local native quarries.

With the primitive oil presses, there is built in one of the walls of the room a recess just large enough to admit the baskets of crushed berries and reaching to the ceiling, with a small cistern below to receive the oil. In the center of the room is a mammoth wooden screw. A large beam extending across the room has one end entering the recess above mentioned, while in its center lengthwise is a screw in which the larger one operates.

Once the olives are crushed and filled into baskets or haircloth, they are placed one upon another in the press recess, the screw is turned around and around by means of a stick of wood run through a hole for the purpose, and the gigantic beam descends, reducing the pile of baskets to half the height, while the oil runs in streams into the reservoir below. This press, being of insufficient strength, does not at once extract all the oil, so the pressed pulp is subjected to a second crushing and squeezing and then packed away in a corner of the room until the olive season is over. It is then ground for the third time and re-pressed.

These primitive devices, while they still exist, are rapidly falling into disuse, as they are too laborious and do not produce as much oil as the more modern ones.

Crude oil shipments from Mexico to the United States for October amounted to 986,616 barrels as compared with 886,245 during October last year, and 1,032,704 during October, 1913.

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*Daily Commerce Report.

CONTINUOUS DETERMINATION OF THE CALORIFIC VALUE OF FUEL GASES WITH JUNKER'S CALORIMETER.*

F. B. LARKIN.†

Junker's Calorimeter, as commonly placed on the market in this country, is provided with thermometers graduated in degrees Centigrade, water measuring receptacles graduated in cubic centimeters, and a gas meter that reads in cubic feet. Thus the B.t.u's. in a volume of gas, measured in cubic feet, are given up to a quantity of water measured in cubic centimeters and therefore weighed in grams, whose temperature is raised a number of degrees Centigrade thereby.

In order to determine the B.t.u's. per cubic foot of gas it is necessary to reduce the temperature range of the cooling water in degrees Centigrade to an equivalent range in degrees Fahrenheit, and to reduce the water quantity in cubic centimeters, or grams, to pounds. A single reduction factor for this purpose may be developed from the relation between the British thermal unit and the calorie: namely, one B.t.u. equals 252 calories. We may then write our equation:

$$\frac{\text{c.c. of water} \times \text{range in degrees Cent.}}{252 \times \text{cubic feet of gas}} = \text{B.t.u. per cu.ft.}$$

From this it will be seen that if the water quantity is made $10 \times 252 = 2520$ c.c., the B.t.u. given to the water by the gas in the corresponding time will be $10 \times$ range in degrees Cent., or he temperature range with the decimal point moved one place to the right, and the B.t.u's. per cu ft. will be this quantity divided by the number of cubic feet of the gas passing the meter during the same interval.

The following special log, based on the above reduction factor, makes it possible to secure continuous determinations of calorific value over periods of indefinite length. Table 1 shows the results of an actual test of illuminating gas. Table 2 is taken from a gas producer test of twenty-four hours' duration where practically continuous determinations were made. A little study of these tables will reveal the fact that the B.t.u. for any period (where the period is the time necessary for 2520 c.c. of water to pass the calorimeter) are obtained by moving the decimal point one place to the right; that the total B.t.u. in the gas burned at the end of any period is the average difference in temperatures of entering and leaving water with the decimal point moved one point to the right and multiplied by the total number of periods; that the B.t.u. per cu. ft. for the various periods will show the fluctuations in the calorific power of the gas; that the total B.t.u. per cu. ft. will show the calorific value of the gas

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*From The Wisconsin Engineer.

†Assistant Professor of Mechanical Engineering in Charge of the Laboratory, Lehigh University.

TABLE I.—TEST OF ILLUMINATING GAS.

	—Temperatures in Degrees C.—						—B. T. U.—		—Water Quantity—			—Gas Meter—			B. T. U. per Cu. Ft.		Pressures.		
Time.	Entering Gas.	Leaving Gas.	Entering Water.	Leaving Water.	Diff.	Av. Diff.	Period.	Total.	Read.	Period.	Total.	Read.	Period.	Total.	Period.	Total.	At Flame in MM H_2O.	Barometer in HG.	Condensation in CC. of Water.
9:52-10	....	..	.....	.....	.....	......	.....	.....	0	....	.....	2.900	....	....	.....	.....	..	......	0
9:54-30	29.2	..	22.17	33.12	10.95	10.950	109.5	109.5	..	2520	2520	3.083	.183	.183	598.3	598.3	12	29,953	..
9:56-40	29.2	..	22.17	33.13	10.96	10.955	109.6	219.1	..	2520	5040	3.265	.182	.365	602.2	600.3	12	.....	..
9:58-45	29.1	..	22.18	33.10	10.92	10.943	109.2	328.3	..	2520	7560	3.450	.185	.550	590.2	597.0	12	.....	..
10:1-1	29.1	..	22.17	33.10	10.93	10.940	109.3	437.6	..	2520	10080	3.633	.183	.733	597.3	597.0	12	....	..
10:3-15	29.2	..	22.15	33.10	19.95	10.942	109.5	547.1	..	2520	12600	3.816	.183	.916	598.3	597.2	12	....	..
10:5-25	29.2	..	22.15	33.10	10.95	10.943	109.5	656.6	..	2520	15120	3.997	.181	1.097	605.0	598.5	12	.....	..
10:7-40	29.2	..	22.14	33.14	11.00	10.951	110.0	766.6	..	2520	17640	4.182	.185	1.282	594.0	598.0	12	.....	..
10:9-50	29.3	..	22.13	33.08	10.95	10.951	109.5	876.1	..	2520	20160	4.336	.184	1.466	595.1	597.6	12	.....	
10:12-5	29.3	..	22.12	33.10	10.98	10.954	109.8	985.9	..	2520	22680	4.549	.183	1.649	600.0	597.9	12	....	
10:14-18	29.3	..	22.11	33.10	10.99	10.958	109.9	1095.8	..	2520	25200	4.733	.184	1.833	597.3	597.8	12	....	
10:16-35	29.3	..	22.11	33.08	10.97	10.959	109.7	1205.5	..	2520	27720	4.917	.184	2.017	596.2	597.7	12	....	
10:18-14	29.3	..	22.10	33.03	10.93	10.957	109.3	1314.8	..	2520	30240	5.099	.182	2.199	600.5	597.9	12	...	
10:21-0	29.3	..	22.11	33.09	10.98	10.958	109.8	1424.6	..	2520	32760	5.280	.181	2.380	606.6	598.5	12	...	..
10:23-7	29.3	..	22.14	33.12	10.98	10.960	109.8	1534.4	..	2520	35280	5.463	.183	2.563	600.0	598.7	12	.....	44
					153.44		1534.4												

TABLE II.—TEST OF PRODUCER GAS.

Time.	Entering Gas.	Leaving Gas.	Entering Water.	Leaving Water.	Diff.	Av. Diff.	B. T. U. Period.	B. T. U. Total.	Water Read.	Water Period.	Water Total.	Gas Meter Read.	Gas Meter Period.	Gas Meter Total.	B. T. U. per Cu. Ft. Period.	B. T. U. per Cu. Ft. Total.	At Flame in MM H_2O.	Barometer in HG.	Condensation in CC. of Water.
6.27	..	..	..	....	....	....	....	...	..	....	....	78.065	.....	.....	.....	.....	..	..	..
6.31	20	..	5.0	21.0	16.0	16.0	160	160	..	2520	2520	79.192	1.127	1.127	142.0	142.0	19	*	..
6.35	20	..	5.0	21.0	16.0	16.0	160	320	..	2520	5040	80.326	1.134	2.261	141.1	141.5	19	*	..
6.39	20	..	5.0	20.9	15.9	15.97	159	479	..	2520	7560	81.465	1.139	3.400	139.6	140.9	19	*	..
6.43	20	..	5.0	21.1	16.1	16.00	161	640	..	2520	10080	82.610	1.145	4.545	140.6	140.9	19	*	13
6.47	20	..	5.0	21.3	16.3	16.06	163	803	..	2520	12600	83.755	1.145	5.690	142.4	141.1	19	*	..
6.52	20	..	5.0	21.5	16.5	16.13	165	968	..	2520	15120	84.894	1.139	6.829	144.9	141.8	19	*	..
6.56	20	..	5.0	21.6	16.6	16.20	166	1134	..	2520	17640	86.048	1.154	7.983	143.9	142.0	20	*	25
7.00	20	..	5.0	21.8	16.8	16.275	168	1302	..	2520	20160	87.210	1.162	9.145	144.5	142.3	20	*	..
7.04	20	..	5.0	21.9	16.8	16.333	168	1470	..	2520	22680	88.375	1.165	10.310	144.2	142.6	20	*	..
7.08	20	..	5.1	21.8	16.7	16.370	167	1637	..	2520	25200	89.542	1.167	11.477	143.1	142.6	20	30	34
			5.1		163.7		1637												

*Assumed.

from the beginning of the test; that the longer the test is continued the more nearly accurate will be the final value; and that the work may be checked from observation to observation to insure the absence of errors.

If local conditions do not permit a range of cooling temperatures sufficient to make the periods of at least three minutes' duration it is advisable to have two men on the job, one taking observations and the other keeping the log. In testing producer gas, if a range of about 15 degrees Cent. be maintained, approximately four minutes will be required for 2520 c.c. of water to pass the calorimeter, which is sufficient time for one man to make and enter all observations, and to make and check the necessary calculations. While it is not an easy matter to read the water of condensation at the end of each period, observations at regular intervals will reveal the hydrogen content of the gas and hence the producer action.

CHARACTERISTICS OF RADIATION PYROMETERS.

The Bureau of Standards will have ready for distribution shortly a paper entitled "Characteristics of Radiation Pyrometers." A careful study of this type of temperature-measuring instrument was considered urgent on account of the extensive use of radiation pyrometers in the technical industries. These instruments are widely used in the temperature control of the various processes involved in iron and steel manufacture, alloy-foundry work, glass, ceramics, and brick manufacture, smelting, gas works, steam generation, lamp manufacture, etc.

Many of the instruments examined show different temperature readings for different focusing or sighting distances. Errors thus occasioned may amount to several hundred degrees. The effect of dirt upon the lenses and mirrors is of serious importance. The question as to whether the pyrometer absorbs all the heat radiation falling upon it is discussed, and the theory of the instrument and the connection of the behavior of the pyrometer with the theoretical radiation laws are given.

The bureau receives a large number of these instruments for tests and standardization from various technical industries located throughout the country. Heretofore this testing required about three days for a single instrument on account of the difficulty in heating a furnace to an exactly uniform temperature. A new method has now been developed which permits a satisfactory standardization of a radiation pyrometer within one hour. Many suggestions are given for minimizing the errors to which the pyrometer is subject, and it is shown that this type of instrument suitably designed, adequately calibrated, and correctly used, is a trustworthy pyrometer having many advantages over other types of temperature-measuring devices, both for scientific and technical use.

FACTORS IN HARDENING TOOL STEEL.*

By JOHN A. MATHEWS and HOWARD J. STAGG, JR.

The phenomena of carburizing iron and hardening it by quenching have been known for many centuries, yet the explanation of hardening steel has not yet been given to the satisfaction of all. Many theories have been advanced and each has its adherents, but one can scarcely say that any generally accepted theory or explanation exists. As recently as this year, two very interesting new theories were advanced at the May meeting of the Iron and Steel Institute of Great Britain.

In what follows we are not so much interested in the theories as in the practice of the art of hardening and tempering tool steel, and we shall confine our attentions to carbon steels, together with some consideration of so-called special steels containing various alloys, usually below 3 per cent. We shall not discuss high-speed steels, nor the many low-carbon alloy steels, primarily of value on account of their tensile qualities, but also, in many cases of limited value for tools, especially those used for hot work. We shall consider the subject, also, from the basis of sound well-worked materials and shall not consider the influence of defects, such as pipes, seams, bursts, laps, burning, etc. The hardening operation itself will give sufficient scope for our thought and attention.

Tool steels are included within the range of 0.60 to 1.50 per cent carbon, but not less than 90 per cent of them fall within carbon limits of 0.75 to 1.35 per cent. They are usually made by the very old crucible process or the very new electric processes, and just now there is considerable discussion as to the relative merits of these methods. As the writers are among the few men in the world who have had practical experience with both processes, we will refrain from discussing their respective merits at the present time to leave a free field for partisans. It is hardly necessary to remark that no mere process is a guarantee of quality; it takes brains, plus a process, to succeed in almost any line of manufacture. This is particularly true of tool steel, which is subjected to so many operations between the melting and the selling stage.

EXPANSION AND CONTRACTION WITH HEATING.

Of great practical importance to the hardener are the volume changes, both expansion and contraction, which occur during the critical ranges of temperature. The permanent changes in dimensions which steel undergoes in hardening are of the utmost interest to the hardener, and associated with these changes is the problem of hardening cracks.

Le Chatelier has studied the phenomena of expansion or dilatation by accurate scientific methods and has divided the changes into three zones of temperature: (a) changes at temperatures below that at which allotropic transformation begins; (b) changes at temperatures above those at which allotropic transformation occurs; and (c) changes occurring within the critical range itself. During the first of these periods from 0 to 700 deg. C., iron and steel expand nearly equally, the amount of carbon exerting little influence. For any iron or steel, however, the amount or rate of dilatation increases with the temperature. Below 100 deg. C. the dilatation is about 0.000011 in., while between 600 and 700 deg. C. it increases to 0.0000165 in. per deg. C. Above the critical range, however, the coefficient of dilatation varies directly with the carbon and is nearly twice as great for a 1.20 carbon steel as for a 0.05 carbon iron. The changes taking place at AC_1 and AR_1, Le Chatelier has not been able to study so satisfactorily. He has found, however, that the dilatation, which increases directly with the temperature up to AC_1, suddenly stops and that instead of an expansion, a marked contraction takes place.

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*From The Iron Age; abstract of a paper presented before the American Society of Mechanical Engineers.

On cooling steel from high temperatures, these changes in dimensions are reversed, although they are not quantitatively equal, nor do they occur at the same temperatures. It is an axiom that heat expands and that coal contracts; but with steel there is a certain critical temperature at which an abnormal behavior is noticed, namely, a sudden shrinkage on heating and an expansion on cooling. The expansion of steel in heating to 750 deg. C. is about ⅛ in. per foot, and when we recall that, in quenching, a corresponding contraction attempts to take place suddenly, it is little wonder that strains are set up that may exceed the ultimate strength of the steel.

What is the relation of the above to overheating, or heating above that temperature at which it is necessary to harden? After passing through the critical range, the expansion takes place at its maximum rate. When steel is heated in such a manner it assumes the shape corresponding to the maximum temperature and on cooling the whole piece tends to return to, or near, its original size. In so doing, the outer, or first cooled, portion is hardened first and forms a hard, brittle, unyielding shell, and the strains set up by the slower cooling interior may either (a) fracture the shell, producing external cracks, especially if the shell be uneven in thickneses; or (b) burst the piece at the center is the shell is of even thickness and strength. This latter occurrence is accompanied by a peculiar appearance of the fracture and frequently and wrongly called pipe.

TIME OF HEATING.

Too much street cannot be laid on the fact that there is a correct length of time for heating and that this time of heating is as important as the temperature to which heated. There are at least two dangers which must be avoided.

First, if the heating be too fast, a uniform temperature does not exist throughout the mass being heated. For example, a die block heated too quickly may exhibit the following conditions: The outer portions may be above AC_1, and expanding at the maximum rate; the intermediate portions may be in the transformation range and contracting; while the inner portion, which is below AC_1, is slowly expanding at the characteristic rate below AC_1. What wonder that steel fractures under such conditions?

Second, grain size depends among other variables under (a) temperature above AC_1, and (b) time above AC_1. If heating be of such a character that the piece is held above AC_1 for an abnormally long time, the crystals may have grown to such an extent that on quenching, abnormal grain size is retained and the result is a weak, if not cracked, piece.

Quick heating in a furnace which is considerably hotter than the correct hardening temperature is extremely bad practice. The difficulty is that the thin parts, corners and edges are liable to attain an overheated temperature before the larger portions of the piece attain the correct hardening temperature, and this overheating of the thin parts produces large grain size, abnormal expansion and tends to produce cracks.

SPEED OF QUENCHING.

If a sample of steel be cooled slowly from above AC_1, the solid solution which has been formed breaks up and precipitates its cementite and ferrite and we have then an annealed steel. If the cooling, on the contrary, be rapid, the solid solution is not given the time necessary to permit the complete dissociation into cementite and pearlite, and we find formed the intermediate breakdown of austenite, known as martensite. If the cooling be intermediate in its speed between extremely slow and extremely fast, we find intermediate microconstituents, troostite or sorbite. The correct constituent, however, in a hardened steel is martensite, and to form this martensite the material must be cooled quickly.

There are several degrees of "quickness" which at once suggest themselves. There is, however, a critical rate of cooling through the range which must be attained before the piece will be hardened. On quenching it is clear that the surfaces of the section are cooled and hardened first. If the mass being cooled is of considerable size, different degrees of hardness are noticed from the outside to the middle. This can be illustrated by the two examples in the table, which, however, are not tool steels. Bars of the analysis shown, 3¼ in. sq. by 18 in. long, were quenched from indicated temperatures. A transverse section ½ in. thick was sawed from the middle and Brinell hardness tests made at equidistant points on its surface. It will be noted that in each instance the corners, or thinnest portions, were the hardest. Next in hardness were the edges, and the decrease in hardness was quite uniform to the center of the bar.

The cooling medium used, its temperature and condition also affect the rate of cooling. Benedicks has investigated this subject and arrived at conclusions of extreme interest. He found that in order that a liquid present in large bulk may exhibit a good quenching power it is necessary: that it should possess a high latent heat of vaporization; that it be maintained at a temperature low enough to avoid too abundant formation of vapor. High specific heat, low viscosity and large heat conductivity all act, it is true, in the direction of quick cooling, but the influence of the two factors last mentioned appears to be of a different and lesser grade than the heat of vapor formation.

The authors have devoted considerable time to investigating numerous commercial media which are in use in typical hardening plants of the country at the present time. The results given are only a small portion of those actually obtained, but they are typical.

TABLE OF PENETRATION OF HARDNESS.

	1	2	3	4	5	6	7	
1......	411	359	321	314	321	359	411	3¼ in. sq. by 18 in.; water, 1,500 deg. F. ½ in. transverse section from middle of length. C, 0.29; Si. 0.09; Mn, 0.65; P, 0.01; S, 0.01; Ni, 3.47.
2......	359	316	297	281	297	318	400	
3......	337	283	283	280	283	295	340	
4......	330	283	280	280	280	283	335	
5......	337	278	283	280	285	298	340	
6......	359	301	297	281	297	301	380	
7......	411	359	337	317	337	380	420	

	1	2	3	4	5	6	7	
1......	359	353	337	317	337	353	359	3¼ in. sq. by 18 in.; oil, 1,675 deg. F. ½ in. transverse section from middle of length. C, 0.49; Si, 0.14; Mn, 0.74; P, 0.015; S, 0.014; Cr, 1.18; V, 0.17.
2......	350	335	325	320	323	327	350	
3......	328	330	320	320	320	327	328	
4......	325	320	316	314	316	320	325	
5......	328	325	320	317	320	325	328	
6......	350	327	323	319	323	327	359	
7......	359	350	328	325	328	359	362	

In attacking the problem, the following method was adopted: A test piece was machined from a solid bar, and a hole drilled through the neck to within an equal distance from each side and bottom of the test piece. Into this hole a calibrated, platinum-rhodium couple was inserted and the leads connected to a calibrated galvanometer. The test piece was then immersed in a lead pot, also containing a thermo-couple to the point A, and the lead pot was maintained at a temperature of 1200° F. When the couple inside the test piece was at 1200° F., and the couple in the lead pot read 1200° F., the test piece was removed and quenched to the point B in 25 gals. of the quenching medium under consideration. At the start the quenching medium was maintained at room temperature. The time in seconds that it took the test piece to fall from a temperature of 1200° F. to a temperature of 700° F. was noted by the aid of a stop-watch. It is clear that immersing the test piece in the quenching medium raised the temperature of the medium. The test piece was then replaced in the lead, heated to 1200° F., quenched into the medium at this higher temperature and the time again taken with the stop-watch. These operations were continued until the quenching media, in the case of oils, had attained a temperature of about 250° F.

A consideration of the results is interesting. Pure water has a fairly constant quenching rate up to a temperature of 100° F., where it begins to fall off. At 125° F. the slope is very marked. Brine solutions have both a quicker rate of cooling and are more effective at higher temperatures than water. The curve does not begin to fall off seriously until a temperature in the neighborhood of 150° F. is reached. Where water at 70° F. cooled the test piece in 60 sec., the brine solutions cooled it in 55 sec. As is well known the oils are slower in their quenching powers than water or brine solutions, but the majority of them have a much more constant rate of cooling at higher temperatures than water or brine.

HARDNESS AS AFFECTED BY MASS.

It has been known for some time that different masses of the same material on being quenched under like conditions gave varying physical properties, but it is only within recent years that the quantitative effect has been measured. The authors give below a few results which, although obtained several years ago, are printed for the first time.

Test pieces 4 in. long were made from the same ingot in sizes increasing ⅛ in. in both breadth and thickness. The smallest was ⅜ in. square and the largest 3¼ in. square. Three ingots of different type analyses were chosen and a series of test pieces made from each. The test pieces were heated in a semi-muffle furnace to a constant temperature for each type of material, quenched, and the Brinell hardness test made. Each series was then drawn to 600° F. in a salt bath and the Brinell tests again taken and then reheated to 1200° F. in a salt bath and Brinell hardness tests again run.

The smaller the sample the greater was the figure of hardness, indicating that the smaller sections are cooled with greater rapidity than the larger, and hence more hardness is developed. The same agencies are at work in tool steel. The larger the mass the smaller the depth of hardness when quenched under similar conditions. Benedicks has shown that for steel of constant mass, the higher the temperature, the greater the rate of cooling. Two of his results will be sufficient to cite:

Weight of specimen in grams.	Deg. C. quenching temperature	Cooling time, seconds.
12.3	845	4.43
12.3	703	5.73

These results confirm our experience that in order to produce the same amount of hardness in a small and large section it is necessary to heat the larger section hotter than the smaller. A commercial application of this phenomenon will perhaps be interesting. The authors were recently confronted with the problem of finding out the correct temperature for hardening tools made from the same steel in sizes varying from 1/16 in. diameter to ¾ in. diameter. In other words a 3/16-in. round will harden at 1395° F., while a ¾-in. round bar should be heated to 1450° F.—a difference of 55° F.

TIME AND DEGREE OF DRAWING TEMPER.

After the hardening operation has been safely performed, the next important step is that of drawing the temper. This operation is necessary for two important reasons: The relieving of abnormal strains set up due to the quick contraction or expansion; the breaking down of the extremely hard and brittle structure of the quenched steel. The authors have seen expensive tools such as broaches, dies, etc., actually burst and fly apart due to the fact that the strains set up in hardening were not relieved by drawing the temper soon enough after the hardening operation. If this paper can impress upon its readers the absolute importance and necessity of drawing the temper *immediately* after hardening, the authors feel it will not have been in vain.

In a properly quenched and hardened steel the hardening carbon, that up to 0.90 carbon, exists in the form of carbide of iron, Fe_3C, dissolved in iron, and the solution is known as martensite. If the steel is hyper-eutectoid, i. e., higher than 0.90 carbon, all that up to 0.90 is dissolved and the remainder exists as globules of undissolved cementite scattered throughout the matrix. The drawing of the temper begins to break down the true martensitic structure and as the temperature increases there are formed intermediate micro-structures between martensite and pearlite, first troosite, then sorbite, and finally pearlite. Professor Heyn has published some valuable results on the decrease of hardness on tempering. The results are expressed in per cent of the original hardness:

100 deg. C.....	2.5 per cent.	400 deg. C.....	70.0 per cent.
200 deg. C.....	14.0 per cent.	500 deg. C.....	87.5 per cent.
300 deg. C.....	41.0 per cent.	600 deg. C.....	97.5 per cent.

Regarding the effect of time on drawing the temper we submit the following: Standard ½ in. round A. S. T. M. test pieces were quenched from constant temperature into the same medium, and the temper drawn in the same salt bath at constant temperature for five minutes, fifteen minutes, etc.:

Elastic limit.	Maximum strength.	Elongation.	Reduction.	Brinell.	Remarks.
228,750	260,137	2.5	.....	425	1550-oil-800 deg. F. 8 min.
201,125	214,562	11.6	45.4	390	1550-oil-800 deg. F. 20 min.
175,000	183,187	12	49.35	340	1550-oil-800 deg. F. 40 min.

Each of these results is the average of four closely agreeing checks. A study of the above table shows that time at the drawing temperature has a marked effect. The act of breaking down the martensite is progressive and not sharply defined. Both time and temperature have their effects.

The greater the initial hardness of the piece, the more marked is the effect of drawing the temper. The piece of 0.25 carbon nickel, ⅝ in. sq., quenched in oil, shows a Brinell of 360; drawn to 1200, a Brinell of 223. The per cent decrease in hardness is 61. The piece 3¼ in. sq., quenched, shows a Brinell of 208; drawn to 1200° F., Brinell 183, showing a decrease in the hardness of only 13 per cent.

CHANGES IN SIZE AND SHAPE.

Thallner states that two kinds of strains are present in hardened steel: (a) those which occur in steel of small cross section which hardens throughout; (b) those which occur in steel of larger cross-section due to unequal change in volume of the surface and interior. The first of these also occurs in steel of larger cross-section, but to the greatest degree on the surface. Thallner also classifies steels as (a) those which become shorter and (b) those which become longer or shorter in hardening. The two classes are not sharply divided. In pure carbon steels, the line of demarcation is about 0.90 carbon. In steels which lengthen, an increase in both length and width may also occasionally be observed and the larger cooling surfaces usually become convex. Thallner cites five crucible steels which he examined as shortening and eight basic open-hearth steels as lengthening.

The tendency of steel is to become spherical by repeated quenchings. Law, working with a square piece of tool steel 3½ in. by ½ in. by ½ in., quenched it 550 times and at the end of this work the piece was nearly round in cross-section. The ratio of length to diameter had changed from 3½:½ to less than 2:1. An equally interesting observation by Mr. Law was that the steel did not lose carbon or change in any way in composition.

Many years ago, one of the authors made several hundred hardening experiments and several thousand measurements to study the change of shape. The materials used were cylinders of steel and tape. Crucible steel alone was examined and the following variables were considered: (a) the effect of original form or diameter upon the diameter after hardening; (b) the influence of carbon on change of form; (c) the influence of initial temperatures at quenching; (d) the influence of length of time of heating; (e) the influence of repeated hardenings, and (f) the effect of annealing previously hardened steels, upon change of shape in rehardening. Obviously when plain cylinders of steel are considered there are four possible changes of shape possible, expansion in length and diameter, contraction in length and diameter, expansion in length and contraction in diameter, and contraction in length with expansion in diameter.

Under the influence of the variable conditions mentioned above, all four changes were actually produced. Steel was also found which expanded in length on first hardening and contracted indefinitely thereafter on repeated hardenings. Another steel expanded in length on two hardenings and contracted on the next two. In a variable carbon series of steels from 0.50 to 1.33 per cent carbon, the magnitude of the change in length after four hardenings increased as the carbon increased. For the same series it was noted that the volume changes were greater when hardening annealed rather than unannealed bars. The increase in length is greater the higher the hardening heat for all carbons. The details of this work would take us too far from the purpose of our paper. The point we wish to emphasize strongly is that it is variable conditions that give variable results. Hence, it is of vital importance that steel be furnished uniform, chemically as well as physically, and it is equally important that the user employ every possible refinement in the handling of his product. It is only under varying conditions of heat, size, time, composition, etc., that the results vary. Constant conditions give constant results.

It cannot be overlooked, however, that constant conditions are not always attainable. The maker of steel cannot control conditions in his customer's shop and the customer cannot control conditions in the steel plant, and the human element must be considered in both.

ZACATON GRASS FOR PAPER STOCK.

Attention is called to the possibilities of zacaton grass in the manufacture of paper in a new professional paper of the United States Department of Agriculture, Bulletin No. 309. Zacaton grass extends from California and Texas southward to the Argentine Andes. It grows most profusely, however, in the mountain regions east and west of the City of Mexico, where it is harvested for the sake of its roots. These are made into brushes of various sorts, and for this reason the zacaton plant is frequently known by the common English names of broomroot grass, wire grass, and rice-root grass. At the present time the tops of the plant are allowed to go to waste. It is from these that there is reason to believe that a satisfactory paper-making material may be developed.

An acre of grass should yield at least 3 tons of tops. The plant is a perennial one, the growth being almost entirely from self-sown seed. Unless checked by fire, cultivation, or the harvesting of the roots, the grass will soon cover a field solidly, and it is not uncommon to find many square miles densely covered with the growth. The range can be profitably gone over for roots every third year.

THE SODA PROCESS—A GOOD PRINTING PAPER.

Laboratory tests of this grass conducted by the United States Department of Agriculture show that it can be chemically reduced to paper stock by the soda process more easily and with less expense than is necessary to reduce poplar wood. The same processes and methods which are employed for the manufacture of pulp from poplar wood are quite suitable for the treatment of zacaton, but in place of the wood-sawing, chipping, and screening machinery a grass duster is necessary.

The paper manufactured from the stock has proved as satisfactory in physical tests as a first-grade, machine-finished printing paper. It has, moreover, a very satisfactory appearance and feeling. For bleaching, however, the experiments showed that more bleaching powder was required than with poplar stock.

The percentage of air-dry fiber obtained from the zacaton grass appears to be somewhat less than that from poplar wood, but practically equal to that of esparto. Forty-three per cent of air-dry fiber was obtained in the government experiments from air-dried grass, while the fiber yield from poplar wood ranges from 46 to 48 per cent.

No estimate of the cost of manufacture is made in the bulletin already mentioned. A rapid increase, however, in the demand for paper and the increasing likelihood that the raw material that is necessary for its manufacture will not be sufficient to meet this demand makes the subject worthy of further investigation by the trade. It has been estimated that the growth of wood in the United States is being removed at the rate of 36 cubic feet per acre each year, while the natural increase is at the rate of 12 cubic feet per acre. In other words, wood is being used three times as fast as it grows. The consequence is, of course, a continual increase in the price of raw material, and the desirability of finding some substitute is obvious.

According to preliminary figures compiled by the United States Bureau of the Census, the cotton consumed in the United States during October, 1915, totaled 500,635 bales compared with 451,899 bales for the same month last year. The cotton on hand at the close of the month in consuming establishments amounted to 1,345,749 bales compared with 715,623 bales at the close of October, 1914, and the amount in public storage and compresses totaled 4,171,474 bales compared with 3,777,469 bales on October 31, 1914. The active cotton spindles during October numbered 31,379,385 against 30,461,320 for the same month in 1914. Linters not included above were 68,944 bales consumed during October in 1915 and 30,102 bales in 1914; 130,031 bales on hand in consuming establishments on October 31, 1915, and 65,174 bales in 1914, and 71,372 bales in public storage and at compresses in 1915, and 41,753 bales in 1914. Linters consumed during three months ending October 31 amounted to 186,274 bales in 1915, and 83,146 bales in 1914. Imports of foreign cotton during October were 13,506 bales of 500 pounds each compared with 12,150 bales for the same month in 1914, and the exports of domestic cotton and linters (running bales) during the month totaled 674,655 bales against 497,132 bales for October, 1914.

The U. S. Consul at Santiago reports that American paints and varnishes are very popular in Santiago de Cuba, both on account of the excellent quality which is usually exported and the low freight rates and preferential duties. Imports of paints from the United States into the whole of Cuba amounted in 1913 to 5,734,922 pounds, valued at $473,327, out of a total importation of 10,206,989 pounds, valued at $769,273. In 1914 the imports from the United States amounted to 5,017,123 pounds, valued at $418,952, out of a total importation of 8,998,102 pounds, valued at $661,213. Imports of varnishes from the United States amounted in 1913 to 82,474 gallons, valued at $70,742, out of a total importation of 96,492 gallons, valued at $86,356. In 1914 the imports from the United States amounted to 64,080 gallons, valued at $56,622, out of a total importation of 72,757 gallons, valued at $66,288.

METALLURGY

VISCOSITY OF PORCELAIN BODIES HIGH IN FELDSPAR.*

A. V. BLEININGER and C. S. KINNISON.

The present work is a continuation of the experiments reported in Technologic Paper No. 30 in which the elongation of porcelain bars, subjected to a tensile stress of 5 lbs. per square inch, was studied in connection with variations in composition and at several temperatures.

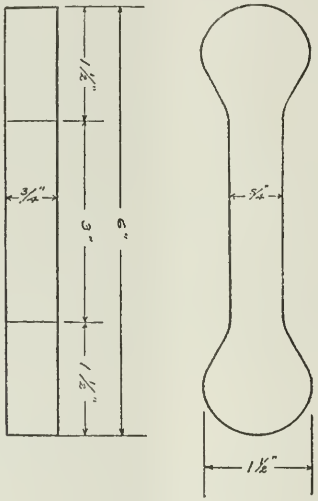

Fig. 1.

The object of the work was to determine the range of compositions showing greatest rigidity, at the highest kiln temperatures, information which should be useful in selecting bodies subject to minimum deformation in firing, and hence causing least loss in manufacture due to deformed ware.

The shape of the specimen was different from the one used in the earlier study and is shown in Fig. 1. This test piece proved to be very satisfactory. The compositions of the porcelains thus studied were intended to include higher feldspar contents and have been compiled in Table I.

The clay content was made up of North Carolina kaolin, Georgia kaolin, and Tennessee No. 3 ball clay in the ratios of 5:1:1. The feldspar used was an average grade of potash spar, and was the same used in the previous work. The bodies were prepared by grinding wet in the ball mill and filter pressing. Plaster molds were used in pressing the specimens. After the pieces were dry, fine shrinkage marks were made on them 4 inches apart. All of the specimens were first burned to cone 10. The fire-clay load pieces to be attached to the lower end of the specimens were made at first to weigh 5 lbs., but it was found that this weight was entirely inadequate, since no deformation was obtained at all. Burns were made then with pieces giving 7.5 and finally 14.5 lbs. per square inch. This weight was adopted as the standard condition for this series.

This shows clearly that the bodies previously studied, containing from 10 to 25 per cent of feldspar, show far less resistance to deformation under tensile stress than the present series with higher feldspar contents. This would appear to be logical from the viscous nature of the feldspar. Several runs, made below 1275° C, showed contraction; elongation due to softening was first observed at this temperature. It is quite probable that contraction and elongation practically neutralized each other within this temperature region. The pieces were hung from fireclay grids, the weight pieces attached and the kiln brought to the desired temperature at the rate of 30° C. per hour. All bodies were vitrified and nonabsorbent. The lengthening of the pieces is expressed in terms of the length after the biscuit burn at cone 10.

TABLE I.—COMPOSITION OF BODIES.

Number.	Clay. Per cent.	Feldspar. Per cent.	Flint. Per cent.
1	35	30	35
2	35	40	25
3	35	50	15
4	35	60	5
5	35	65	..
6	40	30	30
7	40	40	20
8	40	50	10
9	40	60	..
10	45	30	25
11	45	35	20
12	45	40	15
13	45	50	5
14	45	55	..
15	50	30	20
16	50	40	10
17	50	45	5
18	50	50	..

RESULTS.

The results obtained are compiled in Table II, and for bodies Nos. 8 and 18 are shown graphically in Figs. 2, 3 and 4. In the 35 per cent clay series a number of pieces were found to be broken at the higher temperatures, indicating that with low clay content low tensile strengths are obtained. This is to be expected, since in the previous series a load of 5 lbs. per square inch was sufficient to bring about decided deformation. The results, although incomplete, bring out quite clearly the fact that with low clay content high percentages of feldspar are effective in reducing the rigidity or viscosity of the body. At the temperatures involved such bodies are far more subject to deformation than those having a higher clay content.

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*Technologic Paper, U. S. Bureau of Standards.

TABLE II.—ELONGATION MEASUREMENTS.

Number.	Biscuit length.	Length, 1275°.	Length, 1295°.	Length, 1315°, 1320°.	Length, 1345°, 1350°.	Length, 1380°.	Elong., 1275°. Per ct.	Elong., 1295°. Per ct.	Elong., 1315°, 1320°. Per ct.	Elong., 1345°, 1350°. Per ct.	Elong., 1380°. Per ct.
1..	2.56	2.56	2.56	2.62	2.66	*	0.0	0.0	2.3	3.9	...
2..	2.56	2.57	2.59	2.62	*	....	.4	1.2	2.3	...	...
3..	2.48	2.48	2.49	2.50	2.54	*	.0	.4	.8	2.4	...
4..	2.51	2.51	2.53	*	....	....	.0	.8	...	...	...
5..	2.51	2.51	2.53	2.55	*	....	.0	.8	1.6	...	...
6..	2.50	2.50	2.51	2.51	2.51	2.55	.0	.4	.4	.4	2.0
7..	2.49	2.49	2.50	2.51	2.51	2.54	.0	.4	.8	.8	2.0
8..	2.48	2.48	2.49	2.50	2.50	2.52	.0	.4	.8	.8	1.6
9..	2.50	2.50	2.52	2.54	2.54	2.56	.0	.8	1.6	1.6	2.4
10..	2.46	2.46	2.48	2.48	2.48	2.49	.0	.8	.8	.8	1.2
11..	2.49	2.49	2.50	2.50	2.50	2.54	.0	.4	.4	.4	2.0
12..	2.46	2.46	2.48	2.49	2.49	2.51	.0	.8	1.2	1.2	2.0
13..	2.44	2.44	2.45	2.45	2.45	2.47	.0	.4	.4	.4	1.2
14..	2.46	2.46	2.47	2.49	2.49	2.50	.0	.4	1.2	1.2	1.6
15..	2.45	2.45	2.46	2.46	2.46	2.48	.0	.4	.4	.4	1.2
16..	2.44	2.44	2.45	2.46	2.46	2.47	.0	.4	.8	.8	1.2
17..	2.43	2.43	2.45	2.45	2.45	2.46	.0	.8	.8	.8	1.2
18..	2.44	2.44	2.45	2.45	2.45	2.46	.0	.4	.4	.4	.8

From the observations upon the 40 per cent clay series it appears that the greatest degree of softening is reached with 60 per cent feldspar (no flint). The presence of flint increases the viscosity. Of bodies Nos. 6, 7 and 8 the ones containing 30 and 40 per cent of feldspar seem to reach about the same degree of viscosity at the maximum temperature. The greatest rigidity at the highest temperature seems to be shown with a feldspar content of 50 per cent. At 1345° C., body No. 6, consisting of 30 per cent feldspar and 30 per cent flint, is most rigid. Of considerable interest in this set of curves is the fact that three distinct viscosity stages are recognized. At first, softening is observed which at from 1295 to 1315° C. changes to a state of rigidity, since no further elongation is noted. This condition remains constant up to 1345° C., from which point on a decided loss in rigidity is noted and the elongation becomes quite marked. This would seem to indicate further solution of flint and clay for the feldspar, resulting in a viscous magma able to resist deformation. At 1345° the temperature, however, is sufficiently high to bring about softening of the entire mass. According to the viscosity attained between about 1300° and 1345° three classes of bodies may be recognized comprised, respectively, of No. 6, Nos. 7 and 8, and No. 9. The first of these evidently is the most, the last the least rigid within this temperature range.

In the 45 per cent clay series the lowest viscosity (greatest degree of softening) at the maximum temperature appears with 35 and 40 per cent feldspar, the least with 30 and 50 per cent. The body containing 55 per cent of feldspar is in the intermediate position as far as this point is concerned. The greatest degree of early softening is shown by Nos. 12 and 14. The most rigid body up to 1345° is No. 11, and hence it would appear to be the safest as far as deformation is concerned, within the temperature range indicated. A shorter zone zero deformation increase is shown by Nos. 12 and 14. The three viscosity stages mentioned

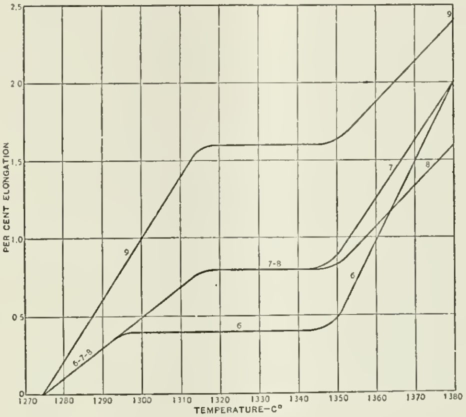

Fig.2

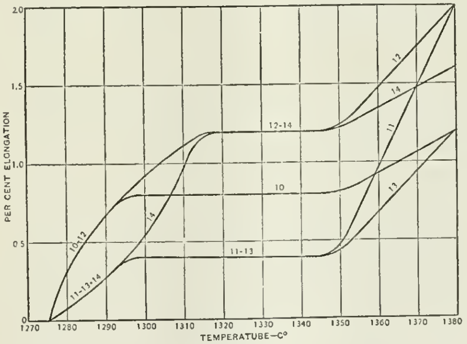

Fig.3

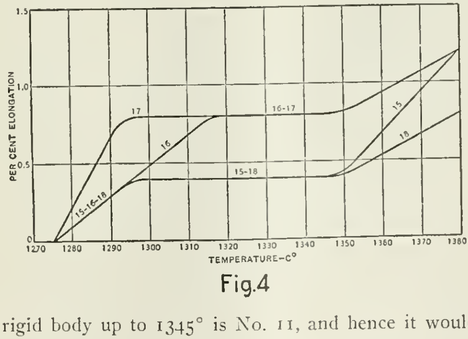

Fig.4

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*Broke.

above are again noted in this series. Between about 1300 and 1345° three classes of bodies may be observed, namely, those of minimum viscosity, Nos. 11 and 13, of intermediate viscosity, No. 10, and greatest viscosity, Nos. 12 and 14.

The far-reaching effect of higher clay content is at once noted in the 50 per cent clay series. At 1380° Nos. 15, 16, and 17 reach the greatest degree of softening corresponding to an elongation of 1.2 per cent, which is very much less than the maximum value for the other series. The system, therefore, by the further addition of clay has become as a whole very much more rigid. The smaller degree of softening is shown by Nos. 15 and 18. The body containing 50 per cent feldspar is decidedly more viscous than the others containing flint. These two bodies and No. 13 are the ones showing least deformation of the entire series of 18 bodies. We again note the three viscosity stages observed in the preceding series and two classes of bodies, Nos. 15 and 18, and 16 and 17.

Collecting the bodies showing the greatest rigidity or viscosity at 1345°, we have the following compositions:

Number.	Clay. Per cent.	Feldspar. Per cent.	Flint. Per cent.
6	40	30	30
11	45	35	20
13	45	50	5
15	50	30	20
18	50	50	..

SUMMARY.

Throughout these series the effect of higher feldspar content was to increase viscosity in a very marked degree, especially in the case of the low clay bodies. This is shown by a comparison of the elongation observed in the first paper published, using a load of 5 lbs. per square inch, with that observed in the present work, employing a load of 14.5 lbs. per square inch. Thus a body with 40 per cent clay and 25 per cent feldspar under a stress of 5 lbs. per square inch showed at 1310° an elongation of 7.62 per cent, while one with 40 per cent clay and 30 per cent feldspar, with a load of 14.5 lbs. per square inch, resulted at 1315° in an elongation of only 0.8 per cent, indicating a viscosity about 11.8 times as great. A slight decrease in viscosity is noted in the 40 per cent clay series when all of the flint is replaced by feldspar. With 45 per cent clay, 35 and 40 per cent of feldspar are most effective in decreasing the viscosity, but higher percentages again increase it. A still higher clay content causes the softening effect of the feldspar to diminish decidedly. Flint in such high feldspar bodies does not seem to be an important factor in governing the viscosity. The greatest rigidity is evidently due to the large clay content, and hence for high temperature porcelains high clay content is essential.

The function of viscosity is not a continuous one. After attaining a certain degree of softening a well-defined rigid state ensues which does not tend to approach further softening until a temperature of 1345° has been reached. Beyond this point the second stage of decided softening is entered upon. Although showing the same degree of viscosity at 1388°, bodies may be divided into several classes, according to the degree of softening observed between about 1300° and 1345°, which seems to be the most useful criterion. High clay bodies having feldspar as the only other constituent show very great viscosity. The most viscous bodies have been assembled.

The results should be of some service in the selection of bodies least subject to deformation in the firing process.

Bitumen Deposit in Honduras.

U. S. Special Agent Garrard Harris reports that there has been discovered in Honduras, on the west coast, in the vicinity of Juticalpa, a deposit of remarkably pure bitumen, or asphalt. Prospects uncovered for over 150 yards show the bed to be of great purity, and there are outcroppings for several miles. The discovery was made by an American citizen, resident in Honduras, who has the control of the property, and who is anxious to interest capital to develop the field. It is considerably distant from the Pacific port of Amapala, which will have to be the port of shipment, but is on the line of a new model road the Government of Honduras is preparing to construct, so that motor transportation will soon be available, and it is not greatly distant from the logical line of the contemplated railroad from Amapala to the interior of Honduras. There are over 15,000 acres in the tract that is controlled by the man who discovered the deposit.

The activity in testing work at the Bureau of Standards, Washington, D. C., has been noteworthy of late. During May 500 hydrometers were tested for the Internal Revenue Service, fifty 100-meter tapes for use of the Government in the Philippine Islands. About 800 tests of thermometers and pyrometers were made. The testing during this spring in the paper laboratory has exceeded all previous periods in the history of the bureau. Two hundred and fifty samples of paper were tested for the Government Printing Office and the executive departments during May and 28 samples for private parties. The bureau has worked closely in touch with the award committees. With the exception of the navy yard, all bid samples of paper submitted under the various supply schedules were sent to this bureau for examination and suggestion. Fifty-two samples of lubricating oils were tested for emulsibility and 17 cup greases were given friction tests for the General Supply Committee. These tests are for the committee's guidance in awarding contracts. Thirty-five water-current meters for use in gaging the velocity of streams were tested in the new meter-rating tank which has lately been put in operation. The recording instruments for the rating station are being constructed in the shop.

DEMORALIZATION IN THE COCONUT-OIL TRADE.

The U. S. Consul-General George E. Anderson, Hongkong, under date of Aug 31, reports that the trade in coconut oil in Hongkong and Far Eastern ports generally has come to be somewhat demoralized, not only as an indirect result of the war but by reason of changes in industrial processes in Far Eastern factories. Incidental to the situation it appears that an attempt on the part of Japanese interests to dominate the coconut-oil market in Japan, and to some extent in other Eastern markets, by obtaining control of the South Sea Islands, whence German manufacturers obtained a large share of their oil previous to the war, has ended, for the time being at least, in more or less disaster.

The chief sources of copra in this part of the world have been the East Indies, particularly Ceylon, Java, and Singapore, the Philippines and the South Sea Islands, such as the islands in the Marshall group. Before the outbreak of the war in Europe the demand for copra was particularly strong in France and Germany, other nations taking considerable of the product but in lesser volume. Most of the copra from the East Indies and the Philippines went to France, while that in the South Seas went to Germany through the organization of the trade of that part of the world possessed by German interests. Considerable quantities went to the United States and to Japan, though it has been more profitable to ship coconut oil rather than copra to the former country. In Japan the industry of pressing oil from copra imported from various points was inaugurated and assumed considerable proportions. The oil made was usually of comparatively poor grades made from the cheapest grades of copra and was mostly used for soap making.

When the South Sea Islands were captured by Japan during the earlier portions of the war their copra was sent to Japan almost exclusively. In the meanwhile the market for oil in Europe was shut off to a considerable extent, and for a time the course of the local copra and oil markets in this part of the world was very uncertain. The high price of good oil at one time led to a number of changes in the trade, and these have become permanent. Oil in the Malay States and the East Indies has been produced at such a rate and by such methods that it can undersell Japanese oil. A low grade "solid oil" imported largely from the Philippines and the East Indies through Hongkong has supplanted the higher grade oil in Japanese, and in Hongkong, Shanghai, and other Far Eastern soap factories.

Singapore and Manila oils are sold, even in Japan, under a special customs arrangement for admitting raw materials under bond, in competition with Japanese-made oil, and naturally control in the Hongkong and other lower Asiatic markets. Clarified and refined fish oil is coming to be used more generally in industrial concerns in the Far East as a substitute for the coconut product. Altogether the coconut oil situation has changed from what it was a year ago. For all that, prices still realized afford ample profit for the modern and properly equipped oil-pressing establishments.

The Hongkong market for coconut oil continues good, though prices have a lower range than anticipated at the beginning of the year. Exports of copra to both Europe and the United States by way of Hongkong have been far below normal.

Philippine copra, heretofore of comparatively low grade because of the manner in which cured, is likely soon to be of the highest grade and to produce the best oil. Philippine copra producers have been agitating for modern "copra centrals," for drying coconuts, similar to the large sugar centrals erected by the Goverment for sugar producers. A Government commission appointed to study processes for drying the nuts is testing various drying machines including machines used by German interests in the South Sea Islands, whence some of the best copra has been received. When a standard dryer has been selected central plants will be established in various parts of the Philippines. It is estimated that by reason of the inferior Philippine product native producers are losing one to two million dollars gold a year. The Philippine government has been endeavoring for several years to improve methods of curing, but with comparatively little success.

FLUORSPAR AND HYDROFLUORIC ACID.

The U. S. consul general at Moscow, under date of June 12 reports that at the conference of agriculturists of the Kieff committee concerning the revision of commercial treaties it was found necessary to organize the production of superphosphates in some part of the southwestern district to meet the requirements of the district in fertilizers. This project was approved by the Kieff zemstvo, which appointed a conference for the discussion of some technical questions. The questions discussed were the following: (a) Whether it is possible to produce superphosphates from Russian phosphorites; (b) whether it is possible to produce double superphosphates from Russian phosphorites; (c) whether it is possible to utilize Russian pyrites for producing sulphuric acid required for the manufacture of superphosphates; (d) whether it is possible to produce superior grades of superphosphates by adding bone dust; (e) to which Russian phosphorite preference should be given as material to be used; (f) to which Russian pyrites preference should be given for the production of sulphuric acid. The majority of the questions were decided in the affirmative, and a number of measures were decided upon for the development of this industry.

PEPPERMINT AND SPEARMINT AS COMMERCIAL CROPS.

The annual production of peppermint and spearmint oil in the United States is estimated by the Department of Agriculture at about 250,000 lbs. out of a total production throughout the world of about 600,000 lbs. Practically all of this oil is produced in Michigan, Indiana, and New York, a little less than 25,000 acres being planted to mint in these states. It is said, however, that there are other localities in which the industry could be profitably developed if there were a greater commercial demand for the oil. At the present time, however, the price of peppermint and spearmint fluctuates widely, and the entire industry would be likely to suffer from over-production if the acreage were to be rapidly extended.

On the muck lands of southern Michigan and northern Indiana where mint culture has become highly specialized, the cost of establishing an acre of new mint and caring for it during the first season is placed at about $30. In subsequent years the cost per acre would be about $15. These estimates do not make any allowance for fertilizers, taxes, interest on the land, equipment, superintendence, and other overhead charges of this character. In Wayne County, New York, where mint is cultivated on uplands, the cost of preparing the land is somewhat less but the tillage costs, on the other hand, are higher because of the greater quantity of hand labor required. The industry in the New York district, however, appears to be declining in extent. It is now carried on in rather a small way chiefly by co-operation between land owners and practical mint growers. In Michigan and Indiana, on the other hand, many of the growers have invested considerable capital in the business and have provided themselves with an equipment which enables them to handle the product in an economical manner.

The yield of oil per acre varies widely, ranging from almost nothing to nearly 100 lbs. About 325 lbs. of peppermint and 340 lbs. of spearmint are required to produce a pound of oil in commercial practice. The price varies as widely as the yield. For peppermint oil in tins, however, the average trade price for the last 40 years has been in the neighborhood of $2.50 a pound, although it has sometimes fallen as low as 75 cts. Spearmint oil, which used to be a little cheaper than peppermint, has averaged for the past 5 years $3.55 a pound. These prices, however, it must be remembered, are somewhat higher than those which the producer would receive.

In Michigan and Indiana the large plantations have of late years installed their own distilling plants, many of which are elaborate and expensive. For growers who do not have their own distilling plants, the customary charge for distilling oil has been fixed for many years at 25 cents a pound. The bulk of the mint grown in this country is distilled in comparatively small plants which serve the needs of several growers.

Both peppermint and spearmint thrive best in deep soils which are rich in humus and retentive of moisture but fairly open in texture and well drained. They may also be grown successfully in well prepared upland soils, such as those suitable for corn or potatoes. The area selected should be summer fallowed for one or two years before the mint is set out, or else it should be cropped with some plant that requires clean and frequent tillage. The tillage is also continued as long as possible during the growth of the crop, for successful mint growing implies clean culture at all stages of progress. The crop is cut at the time of full bloom which, with new plantings, is usually early in September. It is as a rule allowed to dry partially in the field before being hauled to the still. Laboratory experiments show that this results in an appreciable loss of oil, but the loss is not regarded by growers as sufficient to offset the increased cost of handling and distilling the green herb. Exposure to frost, however, must be avoided, as frozen mint yields scarcely one-half of the quantity of oil which could otherwise be secured.

Nitrate of soda, applied at the rate of 50 to 150 lbs. to the acre, and potash have been widely used as fertilizers to stimulate the growth of mint, and potash is particularly useful against a form of chlorosis, due, apparently, to too much water in the soil. On the other hand, ground bone, acid phosphate, and lime do not seem to be of marked benefit. Few diseases and pests trouble peppermint, and spearmint is practically free from them all. During very wet seasons a rust fungus sometimes appears, and crickets, grasshoppers, and caterpillars may always do some damage. On suitable soil and with proper cutivation, yields of from 2 to 3 tons of mint herb per acre may be expected. As has already been said, however, the yield of oil is extremely variable and large yields can only be expected from fields that are in the best possible condition. A fair average for well managed commercial plantings may be said to be 30 lbs. of oil per acre. Since the oil is the chief marketable product, adequate distilling facilities and a market for the oil are essential to success in the industry and the prospective mint grower should assure himself on these points before investing capital in plantations.

The Gazette de Hollande of Oct. 20, 1915, says that the glass industry at Leerdam, Netherlands, in which 1,400 workmen are employed, is threatened with a stoppage as a result of the total prohibition of export of soda from Britain, soda being one of the raw materials in the manufacture of glass. The stock of soda on hand is sufficient for six weeks. Serious efforts are being made to buy the soda in America, but this entails great expense.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

Effects of Selection on Alkaloids in Belladonna.

Under the title "Some Effects on the Production of Alkaloids in Belladonna," the United States Department of Agriculture in Bulletin 306, printed elsewhere in this issue, gives the results of a series of tests on controlling pollination of first and second generation plants with especial attention to cross-pollination and close-pollination. Following are the conclusions reached in the bulletin:

It having been established in the previous investigation that a wide range of variation exists in the alkaloidal content of belladonna plants, the present investigation was undertaken to determine whether the characteristic of alkaloid production is transmissible to the progeny through seed and whether the character is changed by vegetative propagation. The results thus far show that the first-generation plants secured from seed of cross-pollinated selected individuals display the characteristic of the maternal parent with regard to alkaloid productivity. This condition is generally true at all stages of growth during a season and also for at least two successive seasons. Close pollination of the parent plant has shown only a moderate influence on the transmission of this characteristic.

Second-generation plants from cross-pollination have been grown at Arlington, Va., Madison, Wis., and Timmonsville, S. C., and at all three stations they have displayed the relative alkaloid-producing tendencies evident in the original parent plant and the generation preceding.

While the plants at the different localities showed a parallel relationship toward each other, there was considerable difference in the general quantity of alkaloids produced. Thus, in the case of Madison and Arlington, where two pickings were made at fairly corresponding stages of growth, it was found that the Madison plants yielded more alkaloids than those at Arlington. At Timmonsville the yield was still greater than at Madison, but here only one picking was made, and it is hardly possible to make a true comparison. Nothing definite developed to indicate that a relationship exists between the amount of precipitation and sunshine and the percentage of alkaloids produced.

Plants were grown from cuttings, and at two stages of their growth these plants showed a marked tendency to display the same characteristic regarding alkaloid production as the plants from which they were propagated and the original parents of those plants.

Dye Stuffs.

The Japanese Government has voted a subsidy to all corporations engaged in the manufacture of dyes in Japan, provided that more than half the capital is subscribed by Japanese subjects. The subsidy is extended to concerns making every form of dyestuffs and dye chemicals, including aniline salt, aniline dyes, alizarine dyes and synthetic indigo. The amount of subsidy will enable the companies to pay a dividend of 8 per cent on paid-up capital, and will be for a period of ten years. Medicines or perfumery manufactured from coal tar by-products will be regarded as manufactured dyes and chemicals, as well as material for gunpowder.

The latest move at home is the announced incorporation of the Federal Dyestuff & Chemical Co. of New York, with a capital of $15,000,000, said to be the means by which Standard Oil interests and the du Pont de Nemours Powder Co. will enter the dye-making field. It has been understood for some time that large moneyed interests were ready to enter this field if assured of protection after the war by some anti-dumping law as protection from foreign competition; and it is reported that some such assurance has been given by Secretary Redfield.

Great University Laboratories May Assist Business.

In an effort to ascertain to what extent the large universities may co-operate with the representative business establishments of the country in the matter of industrial research, the directors of the Chamber of Commerce of the United States have voted that the questions involved be referred to its committee on education or to a special committee. It was further ordered that the subject be taken up with educational institutions for the purpose of ascertaining the extent to which these institutions may be interested.

In presenting the subject, W. M. McCormick of Baltimore, a director of the National Chamber, told his colleagues that in this country we have permitted each field of industry, each line of education and the national government to pursue alone its course of research. The results obtained have been quite independent of each other. In other countries, Mr. McCormick pointed out, these great factors have worked together along co-ordinated lines to produce economic advantages to business and educational and social benefits of the greatest value to the people as a whole.

A Plea for University Co-operation.—Large industries such as glass making, food, steel and drug manufacturing, Mr. McCormick said, are connected by very slight threads—if connected at all—with the great universities or with the government, except as the government exercises police supervision over the products of the business industries. He believed the Chamber of Commerce of the United States, representing as it does large commercial organizations throughout the country, was in a position to approach the educational institutions and government officials with a view to preliminary conference on the subject. The National Chamber has formed a bond of union between the government and business interests in a way nothing else has done and he believed it would now go a step further.

A Suggested Method of Procedure.—The subject of such co-operation, Elliot H. Goodwin, secretary of the National Chamber, explained in Washington, was brought forth at the scientific section of the American Pharmaceutical Association meeting at San Francisco by Dr. A. R. L. Dohme, of Baltimore. It has been suggested that the National Chamber call a meeting at Washington inviting thereto the presidents of twelve prominent educational institutions and twelve heads of large industrial or manufacturing plants, each representing a different industry. Consideration would be given to the possibility of each educational institution handling specific problems for the industries, making experiments for them if necessary or desirable, and endeavoring to organize a course of study training their graduates along particular lines that would be of direct benefit to the industries. The understanding would be, in this case, that these manufacturers would be willing to eventually take the most desirable of these students into their plants for the working out of the future scientific development and the problems of manufacture.

Investigation of Fusible Tin Boiler Plugs.

The attention of the Bureau of Standards, Department of Commerce, has been directed to the failure and deterioration of fusible tin boiler plugs in service. In some cases such plugs have failed to melt, and so give warning of dangerous boiler conditions, and investigation has shown that the tin filling in these cases had become oxidized to tin oxide (SnO_2), which has a melting point above 2,900° F.

About 1,050 plugs, of which 100 were plugs which had been in service, were obtained through the courtesy of the Steamboat-Inspection Service, Department of Commerce, and subjected to examination. This included inspection of design and construction, condition and purity of the tin filling, and in the case of the used plugs their classification according to the type of deterioration undergone by them in service.

One pronounced and dangerous type of deterioration is the oxidation of the tin along the grain boundaries, by which is formed a network of oxide throughout the tin. This is shown to be due to the presence of zinc in amounts as low as 0.3 per cent.

Lead and zinc are found to be the principal impurities in tin-plug fillings, and since all "failed" plugs contained these or other impurities the conclusion is reached that if these impurities are eliminated by strict specification, which will allow only admittedly superior qualities of tin, such as Banca and some others, the danger of failures of these plugs will no longer exist.

In a monograph on the subject directions are given for the testing of the purity of the tin in such plugs.

German newspapers announce the issuance of a patent to one H. Steffens for making a lubricating substance out of beet-sugar molasses. Commercial Attaché Erwin W. Thompson, writing from The Hague under date of May 1, states that it is not yet known whether the new lubricant is at all practicable, as it is still in the experimental stage; that the normal production of molasses in Germany is about 450,000 tons a year, but that it would be an easy matter largely to increase this output.

WANTED—3 chemists and metallurgists—iron, steel and similar work; $100-$175 per month. H. H. Harrison & Co., Association Bldg., Chicago.

CHEMISTS and metallurgists with industrial and commercial experience. Several good positions open paying between $60-$125. The Engineering Agency, Inc. (23rd successful year), 1662 Monadnock Bldg., Chicago, Ill.

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APPLIED CHEMISTRY.*

By L. H. BAEKELAND.

It is only three years ago that a Brooklyn alderman, who, in the absence of the mayor of New York, had to welcome the visitors to the International Congress of Chemistry, addressed them as if they were druggists or pharmacists.

After all, he made not much greater a mistake than many so-called educated men who obtained a B.A. and yet are ignorant enough of elementary scientific knowledge to imagine that the main occupation of a chemist is to analyze substances and detect falsifications.

Even in England, a pharmacist is currently designated as "chemist," while a real chemist is called an "analytical chemist."

But the European war has done much to correct some of these mistaken notions of the public at large. Our daily press has to a certain extent acquainted this country with the fact that in our national make-up, there are such things as chemical problems. I doubt, however, whether the unthinking masses have begun to realize that aside of the so-called chemical industry, practically every other industry, in fact, every enterprise, has chemical questions to contend with, and that chemical industry itself is intimately interwoven with the great network of every modern industrial or agricultural condition: that the economic welfare of our country, and the health of its citizens is largely dependent on the way we utilize our chemical knowledge.

CHEMICAL WARS.

The present war has been aptly called a "chemical war," because efficient work of every department of the fighting armies, from the Red Cross service to the manufacture of guns and explosives, involves incessantly chemical knowledge and—still more chemical knowledge.

But do not imagine that this is the first chemical war. The art of killing and robbing each other became "chemical" the day gunpowder was invented; at that time, however, the existing knowledge of chemistry was just of pinhead size. Napoleon knew very well how to use adroitly exact knowledge and chemistry for furthering his insatiable ambition to dominate the world; so he surrounded himself with the most able chemical advisers and scientists, and, for awhile at least, he placed himself at a decided advantage over his many enemies; incidentally, he thus helped to lay the foundation for some very important branches of chemical industry.

"Les chiens ont appris quelquechose," exclaimed the Corsican conqueror when he realized that his enemies began to adopt the same means which had given him temporary mastership over them; but those whom he called so contemptuously "the dogs" finally beat him at his own game.

Ever since then, science, technology and chemistry in particular, have played a role of increasing importance in the armament of nations. This accounts perhaps for the strange fact that the really great military inventions have practically all emanated from civilians and from non-military nations like our own. If the men of the military class, essentially conservative in all countries, had been left to their own devices, they would probably still be fighting with bows and arrows —or perhaps, with the traditional sling. Nor should the pacifist blame the chemist if the latter's most beautiful conquests in science, if his proudest discoveries, have been turned into means of relentless destruction and human slaughter. Do not reproach chemistry with the fact that nitrocellulose, of which the first application was to heal wounds and to advance the art of photography, was stolen away from these ultra-pacific purposes for making smokeless powder and for loading torpedoes. Do not curse the chemist when phenol, which revolutionized surgery, turned from a blessing to humanity into a fearful explosive, after it had been discovered that nitration changes it into picric acid.

As well might you curse written speech or language or the art of printing—by which the most noble thoughts of the human race have been expressed, disseminated and preserved—if it has been used also to distribute the vilest lies and the most damnable errors.

Knowledge is like a knife: in the hands of a well-balanced adult, it is an instrument for good of inestimable value; but in the hands of a child, an idiot, a criminal, a drunkard, or an insane man, it may cause havoc, misery, suffering and crime.

Science and religion have this in common, that their noble aims, their power for good, have often, with wrong men, deteriorated into a boomerang to the human race. Our very successes will threaten to devour us as long as all of us have not yet become imbued with the truth that greater knowledge, like greater possession of wealth or power, demands a greater feeling of responsibility, greater virtues, higher aims, better men.

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*Presented at the 51st Meeting of the American Chemical Society, Seattle, Aug. 31 to Sept. 3, 1915.

Let us hope, in the meantime, that war carried to its modern logical gruesomeness, shorn of all its false glamor, deceptive picturesqueness, and rhetorical bombast, exposed in all the nakedness of its nasty horrors, may hurry along the day when we shall be compelled to accept means for avoiding its repetition.

Will you take it amiss if I made a digression from my subject as an answer to some repeated attacks which have been made of late by men who blame our increasing scientific knowledge in general and our chemical science in particular, for the excesses of the present European war?

THE PEACEFUL WORK OF AMERICAN CHEMISTS.

But let us turn our attention to more peaceful chemical pursuits and more particularly to the chemists of this country.

Their work is difficult to understand and still more difficult to be appreciated by the uneducated or uninitiated; nor do chemists court the plaudits of an ignorant public that cannot understand them; they feel fully compensated by the results of their work if it only meets with the approval of a few of their fellow-chemists, irrespective whether it brings them financial results or not; in fact, most chemists are so much in love with their work, that very often they neglect the financial side to their own immediate detriment.

Unlike the physician, lawyer, clergyman, actor, writer, artist, or business man, the chemist does not depend on the public at large; he is either engaged in some private enterprise or he acts in a consulting capacity for a few people, if he is not engaged as professor or teacher in some educational institution. Popularity in the usual sense has little or no value for the chemist.

No wonder then that the chemists of this country, numerous and active as they are, have hardly been noticed among the daily noise of newspaper sensation and shrieking publicity—no more than a skillful watchmaker would be noticed among the hammering of a busy steam-boiler manufacturing plant.

And yet, right here in the United States, the chemical profession has taken such a root, such a development during the later years, that we have here assembled at this very meeting, the representatives of our national American Chemical Society, which counts over 7,000 members, by far the largest membership of any chemical society in the world, with all due respect to England, France and Germany—a society which finds it possible to spend yearly over $100,000 on its three chemical publications, copies of which are to be found all over the world in every well-equipped scientific library. Nor is the study of chemistry in this country a matter of recent occurrence. Our European friends are astonished when we tell them that as far back as 1792, there existed already the Chemical Society of Philadelphia, which was probably the first chemical society ever organized in the world; even today, some of the papers read at the meetings of that early scientific body furnish very interesting reading. Some of our American universities equipped chemical research laboratories for students, at a time when exceedingly few of the best known European universities possessed any such facilities.

Nor should we overlook the fact that notwithstanding the essentially pragmatic tendencies of our country, the United States has given to the world a Willard Gibbs, who outheorized existing chemical theories and whose mathematical deductions are still, after his death, furnishing food for profound thought to the most renowned physical chemists of Europe, to whom they have opened entirely new fields in the study of chemical dynamics.

THE ANILINE-DYE SITUATION.

I mention this more particularly because some of our aniline dye consumers have taken the chemists of the United States bitterly to task and have made decidedly unfavorable comments on their abilities, because since the European war, dyes could no longer be imported from Europe. But Dr. B. C. Hesse, an American-born chemist, a graduate of the University of Michigan, has already ably answered this indictment of the American chemists. In a paper full of information on this subject, which he presented at our last General Meeting,[2] but which, unfortunately, has received little or no attention from our daily press, he has clearly demonstrated that the aniline dye consumers of the United States can have all the chemists and all the dyes they want; provided they are willing to make the necessary investments of capital and to submit to the risk of uncertain profits by starting their own dye-manufacturing establishments here in the United States instead of, as in the past, favoring imported dyes, either through personal choice, or by fostering legislation which forbids the home manufacturers to utilize such methods as selling agreements, "Kartels," or other consolidation of interests, "dumping,"—so as to kill new competitors in the field, while making up the temporary loss by increasing the price of other products,—and in general, any of the many other trade arrangements and trading tricks freely and openly utilized by European manufacturers so as to stifle possible competition of our home aniline dye producers.

The outcry which has been raised as to our shortage of artificial dyes is out of all proportion if we take into consideration that the annual importation of dyes and synthetic products from Germany amounts only to about $9,000,000. As our former president, Mr. A.

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[2] Journal of Industrial and Engineering Chemistry, 7 (1915), 293.

D. Little, pointed out[3] this represents about the same sum of money as the amount of candy sold annually by the Woolworth Ten-Cent Stores.

LOCAL OPPORTUNITIES OF AMERICAN CHEMICAL INDUSTRIES.

The development of any chemical industry is a matter of local opportunities; for instance, the manufacture of cellulose, as well as the industry of wood distilling, have taken a greater development in the wood-covered sections of the United States than in Germany or any other country in the world.

The magnitude and earning capacity of the largest German chemical enterprises, however imposing they may be, look less astonishing if you take into consideration that some of these companies have been in existence for more than half a century. Much younger American chemical enterprises, which make American specialties—for instance, the Eastman Kodak Company, which sends its films and photographic papers throughout the whole world—have annual earnings decidedly greater than the most successful German chemical works of much older existence. Nor is the value of the output of our largest purely chemical companies much less important than that of the German concerns.

SULPHURIC ACID.

This country is now the greatest producer of sulphuric acid with an annual production of about 3,000,000 tons. Yet it is not so long ago that the first maker of sulphuric acid could not even find a purchaser for a trifling small production of a few tons per week. It needed the opportunity of a home market; by and by this was created by the refining of petroleum after the discovery of our oil fields, the discovery of natural phosphates and the resultant industry of superphosphates, the use of dynamite for blasting, the development of the glucose industry, and electrolytic copper refining. These and many other new industries all required large amounts of sulphuric acid, and gave this country an opportunity of developing sulphuric acid manufacturing to its present importance. In fact, the same reasoning holds good for all of our industries. I doubt very much whether the talented foreigners, who have now become proficient in chemical manufacturing, would have tied their initiative and enterprise by specializing in coal-tar dyes manufacturing, if they had had the limitless opportunities of an immense undeveloped country like ours, to which to give outlet to their spirit of pioneership in mining, transportation, agriculture, and similar subjects, all beckoning for more urgent attention, and offering at the same time, more immediate rewards.

AMERICAN ELECTROCHEMICAL INDUSTRIES.

In the meantime some of our other chemical industries, better suited to our local conditions, have taken such an enormous development here as to make the United States an undisputed leader in at least some of them. Such products as the various acids and salts, aluminum, artificial abrasives, soda and caustic alkalies, bleaching powder, chlorine products, electrolytic copper, are decidedly more important in value and in economic importance than the few million imported coal-tar dyes.

Mr. F. A. Lidbury[4] pointed out rightly that if there had been a shortage in some of the products of our electrochemical industries in which the United States has been a pioneer, the consequences to our national economics would have been so serious that the present complaint of our aniline dye users would have sounded like a timid whisper, compared to the bellowing lamentations of so many more important industries which would have become absolutely paralyzed. The fact is that few men realize how many industries are directly dependent on the work of American chemists. If the aniline dye industry has been somewhat neglected in this country, there are many other good reasons for it; not only was the possibility of reasonable profits too scant to offer special inducement to clever-headed business men to risk their capital in this branch of manufacturing when they had so much better choice in other channels of enterprise, but the first raw material, suitable coal tar, was not abundantly available here as it is in Europe, for the simple reason that this country long ago discarded the older and more expensive methods of gas manufacturing generally used in Europe, and which give coal tar as a by-product. The less expensive and simpler water-gas process, adopted in the United States, gives no suitable gas tar; it is only of late, by the introduction of the by-product coke ovens that we can look forward to an almost unlimited supply of coal tar.

In the meantime, the German manufacturers had every opportunity in specializing in these coal-tar industries and could afford to concentrate their efforts so as to supply not only their home consumption and that of the United States, but that of the whole world; in about the same way as the United States sends to the remotest corners of the globe its sewing machines, its typewriters and its Ford cars.

Judging from the past history of the chemical industry in America, I have little doubt that the day it will be found profitable to manufacture all kinds of synthetic dyes here in the United States, instead of a few as is the case now, there will be little further delay in supplying the demand by a hustling and bustling home production.

In fact, it is quite possible that under present abnormal conditions, this branch of manufacturing may be stimulated to the point as to result in overproduction after the war is over.

CHEMICAL RESEARCH IN UNITED STATES.

If hitherto our chemists have been deficient in this special line, we can, with some satisfaction, point to better efforts in other chemical industries. For instance, it is not sufficiently known how many research chemists in our different American manufacturing establishments are busily occupied in studying and improving manufacturing processes, nor what large sums of money are devoted every year to industrial chemical research. If we hear it constantly repeated that some of the largest German chemical companies have hundreds of chemists and engineers, it is less known that right here in the United States, the number of chemists employed in some of our better organized chemical enterprises is scarcely less; but nobody finds it necessary to boast about it. In fact, the most striking symptoms is that so many engineering enterprises, for instance, some of our large electrical companies—although their field of action seems rather remote of chemical subjects—have now elaborate chemical research organizations, of which the record is well known by their excellent results.

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[3] Ibid., 7 (1915), 237.

[4] F. A. Lidbury, Metallurgical and Chemical Engineering, 13 (1915), 277.

Conditions were quite different some fifteen or twenty years ago; but this country has grown, and as the requirements and opportunities grew up at the same time new chemical problems arose thereby.

THE ANALYTIC AND CONSTRUCTIVE TURN OF MIND.

The urgent nature as well as the magnitude of some of these new chemical problems, is shaking our chemists awake,—is making new men of them.

Professor Whitaker is probably right when he says that the chemists are thirty years behind the engineers as far as method and attitude of mind is concerned, but this same criticism holds good for chemists all over the world. The fact is that the engineer was called first, and he was born centuries before the chemist, but the latter is now making up for lost time.

New conditions, new problems, are compelling the chemist to learn to tackle a proposition in a true engineering spirit and—to hitch some business sense to it. He is learning to forget thinking or acting on the test-tube plan; he is thrown more and more in contact with business men; he begins to realize that too one-sided theoretical considerations are sometimes more dangerous than complete ignorance and that a sense of proportion and relative values is the first requirement for good practical effort.

Here, indeed, is one of the weakest spots of the chemist. Aside from the fact that the chemical profession seems one of those vocations which have fascinated a large number of intellectual freaks, it has generally attracted men of an analytical, rather than a constructive turn of mind. Successful engineering is essentially constructive. The most urgent work for the chemist of to-day must be constructive—he must learn how to cement together the vast amount of data which already lie at his disposal, even if he, himself, has to provide this very cement by further research.

THE CHEMIST IN OTHER INDUSTRIES.

The chemist of today is no longer confined to purely chemical enterprises; even the most stubbornly conservative manufacturers have learned, through competition, that every industry, however mechanical be its nature, has its chemical problems. Things have changed rapidly since the day Andrew Carnegie listened with a sly twinkle in his eyes to the fun his competitors were poking at him when he first engaged a spectacled professor to investigate the chemical problems in his iron works. Conditions have now become reversed; today, a steel or iron works without a competent chemist justly provokes contempt and distrust.

Nor is the time so far distant when even our biggest railroads had not begun to realize how they missed the constant services of a staff of chemists, so as to advise them in the endless chemical problems which present themselves in the operation of a well-organized railroad.

Some time ago, I visited the plant of the National Cash Register Company, in Dayton, Ohio; one of its most interesting departments was its well-equipped chemical laboratory, where no end of chemical questions relating to the manufacture of purely mechanical devices have to be studied and solved.

No up-to-date motor-car works is complete without its chemical department and the same remark holds good for all well-organized engineering concerns.

In this country, the importance of chemistry has been first appreciated in its relations to agriculture. So obvious was this, that we set an example to all other nations of the world by the number of our federal and our state chemical agricultural laboratories. This, more than anything else, was the entering wedge of applied chemistry in this country, which extended later on in the Government Service, Geological Survey, Bureau of Standards and the Bureau of Mines. Nor did the useful effect stop there. Many of our federal chemists, our state chemists, have left public service to accept better-paying positions in private industries; but the men trained in public service implanted their high aims and scientific ways in some of our commercial enterprises which needed it badly. I know of some cases where this beneficial influence changed radically the whole spirit of the commercial organization, from its manufacturing to its selling department, and introduced instead of reckless, sordid commercialism, a spirit of fairness and efficiency which soon proved the more profitable policy.

ETHICS OF THE CHEMIST.

In this and similar directions the chemist can exercise a valuable moral influence on the community. If you think it over, you will find that the quest of efficiency lies quite close to the path of honesty, justice and equity.

Here also the chemist has much to learn. In some instances, I have been astounded at the almost childlike attitude of mind of some of our chemists who are too ready to sell their services to anybody who has a temporary use for them, irrespective of the underlying motives or purposes.

Some lawyers tell me that they never have the slightest difficulty in hiring chemical experts to defend contradictory opinions. It is quite amazing how some chemists in their eagerness of pleasing their employers will overlook their own ignorance of the most elementary principles of patent law, as well as their superficial acquaintance with the many details of intricate technical questions while not hesitating to furnish cocksure opinions which encourage infringers or industrial pirates to trespass on the rights of intellectual property of others. Much ruinous patent litigation would be avoided in this country, and invention would be better encouraged if we had more men of the type of a well-known British electrical expert, who never hesitates in court to tell the simple and direct truth, regardless whether it kills or saves the case of his client; his statements are so highly valued and respected that the judges accept them without suspicion, and the same expert is frequently retained by the two opposing parties, whom he serves impartially, and who gladly pay him higher fees than to a mere litigation-acrobat-expert, or a chemical "ambulance-chaser."

EMPLOYERS AND EMPLOYES.

The ethics of our profession have been dealt with by the American Institute of Chemical Engineers, and have been embodied in its recently adopted Code of Ethics, which may furnish a good guide for younger or less-experienced chemists. And this leads me to state that many more manufacturers or business men would be induced to utilize the services of chemists, if they could feel confident that in so doing they are not putting themselves at the immediate mercy of a stranger, by confiding to him facts or processes which it has cost them many sacrifices of time and money to accumulate, and the undivided knowledge of which constitutes sometimes one of their most valuable assets. On the other hand, a chemist can hardly be of any service unless his client or employer is just as frank with him as he would be with his lawyer or physician. However, this mooted point is easily overcome by referring to the Code of Ethics to which I have just alluded, or, better, by making a preliminary agreement between the chemist and his client or employer, safeguarding the interests of both parties. But in such a case, the compensation to the chemist should be made commensurate to the occasion.

This same principle holds good in the employment of chemists in manufacturing plants, where the chemist is either engaged in research or in a manufacturing capacity. An employer should not expect an intelligent chemist to render him important services without proper compensation, and in as far as the practical value of the work of a chemist can seldom be determined in advance, it will pay the employer to offer special inducements or rewards for initiative; he can well afford to give his chemist some share of the increased profits he has received through his work; to do otherwise would be narrow-minded, short-sighted, and detrimental to the direct interests of the employer. The work of a research chemist cannot be performed nor measured like that of a bookkeeper or a laborer; the results of his work are uncertain; delays and obstacles beset him at every turn; sometimes luck plays an important role; but good-will, enthusiasm, and persistent endeavor are indispensable factors and these may be encouraged or killed by the attitude of the employer. An employer who is unfair, or who cannot arouse the respect or the enthusiasm of his chemists, cannot get the best there is in them. He must make them feel that if their work turns out well for him, they will get some decent share of compensation. Therefore, a reasonable salary ought to be supplemented by the possibility of a bonus or some share in the profits based on the earnings brought about directly by the work of the chemist.

On the other hand, the chemist must not overlook the financial sacrifices and business risks assumed by his employer. He should specially bear in mind that knowledge or experience gathered at great cost by his employer, or through expensive factory equipment, or other facilities, have in most cases enabled him to take up his own work at an advanced stage. It would be rather unfair, unless otherwise stated, that a chemist should be allowed during or after his period of employment, to divulge or take advantage of all knowledge or information gathered around the plant in which he is engaged; or patent for his exclusive benefit, any inventions he may make on those particular subjects for which he is engaged, as long as the stimulating ideas themselves have been gathered by the very means put at his disposal by his employer. All these questions should be provided for and embodied in an equitable contract which will necessarily vary with special circumstances. But here again, niggardliness, or too great cunningness of the employer, will hardly pay. Unless his chemist be a fool—and a fool of a chemist is not worth anything—he will lose the good will and confidence of the very man whose work is primarily dependent on these factors.

Faithful and generous observance of these conditions have brought about the most excellent results in many instances. I know that the contract system, with a salary supplemented by a bonus, or participation in profits in special departments, has been used with great advantage to all concerned, by some of the most successful chemical companies in Continental Europe, and in some of the more progressive American enterprises.

It has been objected that a contract of the kind merely binds the employer who has tangible assets, while in most cases it would be difficult to enforce it against faithless employes. But even then, a clear and well-defined contract will prevent many misunderstandings which will crop up in the course of time. It has been my experience that direct dishonesty and faithlessness are merely exceptions among chemists, whatever their other shortcomings may be.

THE CHEMIST AS A RESTLESS PROSPECTOR.

We know where the work of the chemist begins.

We can never tell where it ends, and through what unexpected ramifications it may lead. It is just this fact which adds some zest to the life of the struggling, hard-working chemist, and brings to his work frequently as much excitement as the best of sports; his hopes and disappointments can be compared to those of the restless prospector.

Pasteur, while he was professor at the University of Lille, was consulted by a local alcohol distiller about some irregularities in the fermentation processes. Little did the great French chemist dream, when he tried to solve this purely industrial problem, that by doing so he was going to establish such an amount of new and unsuspected scientific facts, destined to upset all formerly accepted notions, not merely on fermentation, but on life, disease, contagion and epidemics; that he was about to revolutionize surgery, sanitation and medicine, and create several new departments of medical science; that he was going to save millions of lives, reduce sorrow and misery. So little were the men of that period prepared for all these stupendous revelations that this great benefactor of the human race had to suffer most from the gibes and violent attacks of some of the best-known men of that very medical profession into which he was going to infuse new life by placing it on a true scientific basis. The history of the stubborn polemics and angry discussions at the French Academy show that, at that time at least, the imagination even of men of science could not expand to the point of perceiving that medicine and surgery were to be remodeled by the hands of a mere chemist.

According to the Oct. 9 report of the American Association of Commerce and Trade, Berlin, Germany's steel production made a further increase during August amounting to 1,157,692 tons of 2,204.6 pounds against 1,138,651 tons in July, although in the latter month there was one additional workday. This is the largest output since the beginning of the war. The average daily output in August was 44,527 tons, as compared with 42,172 tons in July. The quantities of the different grades produced in the last two months were:

Grade.	July, 1915. Tons.	August, 1915. Tons.
Thomas	563,682	563,358
Bessemer	13,285	14,931
Basic Siemens-Martin	455,778	468,047
Siemens-Martin	23,173	28,721
Basic steel castings	45,838	41,927
Steel castings	15,994	19,345
Crucible	8,555	8,720
Electro	12,046	12,643
Total	1,138,651	1,157,692

Corundum mining in the United States has ceased, while Canadian production dropped from $230,091 in 1912 to $72,176 in 1914. Artificial abrasives have displaced the natural products.

POSSIBLE SOURCES OF POTASH IN AMERICA.*

By FRANK K. CAMERON, Ph.D.

INTRODUCTION.

The absolute value of the potash market in the United States under normal conditions is relatively small, when compared with that of many other products, being in the neighborhood of $12,000,000. Its importance is very great, nevertheless, for potassium salts are almost a necessity in the production of some of our crops, and are desirable in the production of practically all of them. There are other than agricultural uses where the consumption is much smaller, but where the necessity is even more pronounced, as in the production of certain types of soap and certain kinds of glass. Normally this country obtains about a million dollars' worth of potassium nitrate, nearly all of which comes originally from India, although not always directly. Practically all of this potassium nitrate is used in making fireworks and certain types of powder.

As matters stood before the present European conflict, the consumption of potassium salts for military explosives was insignificant. But it is one of the surprises of the war, even to chemists who are not also experts in military matters, that the conflict has brought about such a tremendous demand for types of munitions in which potassium seems to be a necessary constituent, for which there appears to be no satisfactory substitute. Aside from potassium nitrate, as all the world now knows, the whole world's supply of potassium salts came from Germany, from the famous Stassfurt region and from the less well-known Alsatian deposits of rapidly-increasing commercial importance.

The controversies of the year 1909-10 between American importers, the German Kali Syndicate (a selling agency under Imperial supervision), and certain independent producers in Germany led to diplomatic exchanges between the Government of the United States and the German Imperial Government which served at least one good purpose in focussing attention in this country upon the desirability of developing native sources, a desirability confirmed and made more insistent by the unhappy predicament now confronting us. Governmental investigations have been actively in progress since and private initiative has been greatly stimulated. As a result, it has been shown that there are a large number of possible sources of soluble potash salts within the United States, some of which are quite valuable possibly to particular owners, and three and possibly four are potentially possible sources of large commercial importance. At the present writing there is a very small amount of potash salts on hand. The munition manufacturers have been and are still buying eagerly. They prefer the chloride to the sulphate, which is interesting for at least two reasons; it gives a clue to what they are doing with the potash, and it has brought the price of potash, unit for unit, to a higher price in the chloride, though normally the reverse is the case, the sulphate being more highly valued for fertilizers and the chemical industries generally.

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*From the Journal of the Franklin Institute.

No one seems to have any idea, even approximately, as to the aggregate amount of potash salts now in the hands of fertilizer manufacturers and brokers. But it is very clear that the rapidly diminishing imports have about reached the vanishing point, although the world has been scoured for existing stocks, and purchasers for the United States have been as far as Batavia, Borneo. From very recent events it is rather convincingly evident that the embargo on supplies from Germany is not to be lifted until the end of the war. From this point about everything one can say about potash salts is highly speculative. It seems reasonable to expect that prices will be much higher after the war than before, unless workable sources are developed outside of Germany, for potash salts form one of that country's resources that can and probably will be made to shoulder a very large part of the war's expenses. For this reason the ultimate ownership of the Alsatian deposits is of particular interest to the world at large. The Galician and Spanish deposits, as well as those reported from Peru, are possibly of importance, but the information concerning them that is now available offers very slim hopes.

In so far as the technical features are concerned, it has been demonstrated that the United States can produce far more than its own needs in potash salts. Undoubtedly the technology is susceptible of improvement, and of possibly very great improvement. But the potash can be produced, and the real difficulties in the way of a realization of potash production in the United States are purely commercial and not physical.

FELDSPAR.

Of the several possible sources, attention naturally is commanded first by the potassium silicates, such as orthoclase, muscovite, sericite, or leucite, of which large deposits exist in many regions of the country carrying ten per cent or more of potash (K_2O). There are probably a hundred patented processes for the extraction of potash from such materials, all of which processes fall into two classes. In the first class the spar, or other silicate, is mixed with coal or coke, lime, calcium chloride, sodium chloride, nitre coke, or some combination of these substances, and heated to form a sinter, from which the potash salt is leached. To evaporate the leachings another supply of heat is required, and the final product is never the pure potassium salt, but a mixture with other less desirable substances. To recover all the potassium salt in a pure state by crystallization methods alone is impossible, and to recover it by further chemical manipulations is prohibited by the cost. To meet these objections, the second class of processes has been devised in which the original mix is heated to melting, and thus the potassium is volatilized either as the oxide or as the chloride. Some of the proposed methods have now been tested on a sufficiently large scale to demonstrate their practicability, so far as the physical factors are concerned, and one of them has actually produced a few tons of potassium chloride and oxide.

It is claimed by promoters of these processes that there are known large deposits of spar or other potash silicates which can be worked on the steam-shovel plan and which will yield "run of the mine" material containing ten per cent or more potash at a low working cost. Usually these costs of producing the raw material have been stated to be in the neighborhood of $1.50 per ton. These claims may, in some cases, be valid, but it is difficult to find a disinterested authority who thinks that there is a deposit from which ten per cent potash spar can be obtained on a commercial scale without hand cobbing. This would make the cost of production prohibitive, and apparently no disinterested investigator considers it practicable to work a product that approximates ten per cent or more potash. But, in all fairness to the promoters of potash from feldspar, it should be said that the case is not a proved one, either for or against them, in this regard at least.

Again, every disinterested investigator seems to be convinced that potash from feldspar or other silicate mineral is commercially impossible under normal conditions of the market unless the by-product or residue is salable. So far there seems to be but one practical suggestion: to utilize the residue in making cement. Apparently very good cements can thus be prepared, in some cases cements of very desirable special qualifications. But the cement industry is a large one, worth many times the potash industry. It has grown very rapidly and is now standardized. Practically all cement is now sold under standard specifications, which are not met by the feldspar cements without reference to their intrinsic merits. The cement manufacturers, therefore, are not and can not be expected to be willing to remodel their plants, retrain their operatives, secure, if that be possible, a source of spar, and reëducate the buying public, thus risking the larger and sure business on the chance only of securing a much smaller one.

Certainly one, and, if newspaper reports can be trusted, several cement plants are now actually recovering and marketing flue dust containing a relatively high percentage of water-soluble potash. At the abnormally high prices which the product now commands such flue dust can profitably be collected and prove a godsend to certain consumers of potash salts, as, for instance, the manufacturers of liquid soaps. It is very doubtful if these dusts could maintain a market under normal trade conditions.

DESERT BASINS.

All desert basins, speaking generally, contain considerable stores of water-soluble potassium salts, but usually so mixed with insoluble fill derived from the rim rock as to be quite impossible as commercial sources. A very large number of the desert basins have now been explored more or less thoroughly, and, with one exception, it can now be said that the chance of finding a segregated deposit of potassium salts capable of being exploited commercially is a "miner's chance" only, and a poor one at that. Searle's Lake, in San Bernardino County, California, is, in the ordinary weathers of the desert, a mud flat, but below the surface the solid material is mixed with a brine carrying five or six per cent potash in the form of the chloride, mainly. But there are large percentages of other soluble substances present—sulphates, carbonates, and borates, as well as chlorides of sodium and magnesium as well as of potassium. It is impossible, by crystallization methods alone, to recover all the potassium from such a brine in anything approximating a pure salt or a mixture of potassium salts only, and the expense of other methods of separation would undoubtedly be prohibitive. It is possible that a segregation of the potassium might be accomplished with a partial elimination of other salts. A large expenditure, reported to be upwards of a million and a quarter dollars, has not yet resulted in a commercial production from this source. One crystallization procedure has been tried out on a large scale and abandoned. It is reported that the present occupants of the site, the Trona Company of California, are trying out another process, the essential features of which are a saturation of the brine with carbon dioxide and the freezing out of carbonates and biborates by reducing the temperature of the mother liquor with an ordinary ice-making outfit. The scheme is an ingenious one, but its practicability in the middle of a large desert seems questionable in the absence of fuller details of this company's plans.

Another difficulty menacing the production of potash salts at Searle's is the validity of the titles of the present possessors. The Trona Company is controlled by a British corporation, the Consolidated Gold Fields of South Africa, and its holding is the largest ever taken over in the United States by any one individual or company, consequently protestants have arisen, and it is claimed that the original patents on which the title rests were obtained fraudulently. Interested parties claim the possibility that the title of the Trona Company will be rejected and the site withdrawn from entry, pending the passage by Congress of a leasing law. Be this as it may, the uncertainty has hampered, and is hampering, the development of the property. It seems to be the best opinion of disinterested investigators that, ultimately, Searle's Lake may be worked as a source of trona (sodium bicarbonate), with borates and potassium salts as byproducts. The production of potassium will be relatively small as compared with the country's needs. Opinions differ as to the probable grade of the potassium salt. The present writer thinks it must be a low-grade one.

ALUNITE.

Near Marysvale, Piute County, Utah, there is a large deposit of massive alunite, an insoluble mineral, with the composition of a basic potassium aluminosulphate. It is quite similar in composition to alum, hence its name. Other occurrences of alunite in the United States are known, but this is the only one where the mineral occurs in such form and such quantities as to make it a commercially workable proposition. When roasted, sulphur dioxide and sulphur trioxide are volatilized, and, if the residue be leached, either alum or potassium sulphate is extracted, depending primarily upon the temperature of the roasting. The Roman alum, long a commercial product, is thus obtained from Italian alunite, and it has been reported that deposits in Spain, Italy, Australia, and Japan have at times been small producers.

The technical difficulties in producing potassiums from alunite are not serious. But the deposit is located in a forest reserve. The oxides of sulphur, if allowed to escape into the air, may damage vegetation and bring objection from Federal authorities. If condensed and discharged into the streams they will be a menace to fish life, and thus bring objection from State authorities. Sulphuric acid produced in southern Utah has no obvious market in normal times. Hence what might be an asset in some localities bids fair to be a serious charge on the working of the Utah alunites. The residue, after leaching, is a very fair grade of alumina, and possession of a large source of alumina has long been a fairer vision to the lay chemist than ownership of a gold mine. However, there is but one large purchaser of alumina in the United States, and this purchaser has spent great energy, time, and money in securing to itself the more important deposits of bauxite. Hence it cannot be expected to look with enthusiasm upon the development of another considerable source of alumina. For the Utah operators to undertake themselves to produce aluminum appears to be impracticable, for reasons which need not be discussed here. Other possible uses of the alumina are receiving serious attention, but are as yet of doubtful importance, as a sufficient outlet for the quantity of material for which disposition is desired.

The most serious difficulty affecting the production of potassium sulphate from alunite is the transportation problem incident to the geographical location of the alunite deposit. The sulphate of potassium is the form most favored by agricultural authorities, it is true, and in normal times this is the form of "potash" which should command the readiest and largest market. West of the Mississippi River the citrus region of southern California is the only important market in the United States, and of especial interest because it will not use chlorides, but readily takes a fair amount of the sulphate. Hawaii and Japan are certainly possible markets to be considered. The mountains of southern Utah are about as unfortunate a location as could well be imagined, since the potassium salt must expect a long rail haul to any important market.

In spite of these difficulties the exploitation of the alunite has been progressing. By far the major part of the material is in the control of two holders. The Mineral Products Company, having close affiliations with one of the largest fertilizer manufacturers in the country, has established a small plant near Marysvale and has recently produced potassium sulphate on a commercial scale. It is too soon, perhaps, to form any definite opinion on the probable success of this venture. The European war has introduced factors which are difficult to evaluate, and, moreover, the entire output of the venture is in the hands of one purchaser, so that the crucial test of the open market is not available.

The Utah Potash Company, a recently-organized corporation for the working of the alunite deposits on the holdings of the Florence Mining and Milling Company, is maturing plans for a large installation near Marysvale, proposing to work under the Morgan patents, roasting the alunite with lime, whereby a lower temperature can be employed profitably and the escape of the objectionable oxides of sulphur is prevented. The plans of this company are predicated on the experience of copper, gold, and other mining ventures where a low-grade ore worked on a large scale is often very profitable when it is a commercial impossibility on a small operation. In fine, potassium salts have been produced from alunite in the United States, and there is a very good promise that they will continue to be produced from this source, even when they come into competition with the German salts following the close of the war.

Among the considerable number of sea algæ on the Pacific Coast of North and South America occur four species which are peculiar to that coast and which have the power of absorbing from the sea-water exceptionally large quantities of potassium. Of these four algæ, or Giant Kelps, as they are known locally, *Macrocystis pyrifera* is undoubtedly the most important. It reaches its best development south of Point Sur, on the California coast, and north of the Cedros Islands, off the coast of Mexico, where it occurs in large beds or groves from a few acres in extent to fifteen square miles or more. The entire kelp beds along the coast of the United States and Alaska aggregate 400 square miles or more, and could be made to yield annually, under careful harvesting, some six or seven times the normal demands of the United States. The California beds alone could easily produce more than our present normal requirements.

The *Macrocystis* plant, when freshly harvested, contains from three to five per cent potassium chloride. The oven-dried plant will average probably sixteen per cent potash (K_2O) in the form of chloride. The dried plant also contains something less than two per cent nitrogen, and, being fibreless, it goes to pieces in the soil quickly and readily. Pot and garden experiments with dried kelp have shown it to be an excellent fertilizer as compared with equivalent amounts of the ordinary soluble potassium salt.

Harvesting of kelp on a scale comparable with commercial conditions has now been done by a sufficient number of different investigators to have definitely demonstrated the practicability and low cost of the operation. The cost of drying artificially the harvested product has not been worked out so satisfactorily, but enough has been done to show that it is very probably feasible as a commercial operation when the technology of the operation has been adapted to the peculiar characteristics of the material adaptations which will speedily come with more practice and actual contact with the material. Apparently a modern rotary drier is the type most promising, since the wet kelp, when heated in a furnace where a stirring is not provided, quickly mats down to a sticky mass, from the surface of which potassium chloride may be volatilizing, while at the same time the wet interior is at a temperature quite durable to the hand.

While dried kelp is itself a good fertilizer and seems admirably adapted to use in mixed fertilizers, and can probably be produced at a cost which would insure a good profit on the basis of before-the-war prices, it is possible that kelp ash may be more worthy of consideration for the Eastern market. In this material, naturally, there is no nitrogen, but there is about sixty per cent potassium chloride, the remainder being mainly sodium chloride. But it is as a source of pure potassium chloride that kelp has the most promising future. The kelp ash contains, when not too severely burnt, very little soluble material other than potassium and sodium chlorides. Theoretical deductions backed by laboratory experiments have shown the feasibility of a separation of true salts by treating a fixed mass of water with easily calculated amounts of the particular ash, at alternate temperatures, whereby there is a practically complete recovery of the potassium chloride in a nearly pure condition. The writer's own observations and studies have convinced him that these giant kelps offer by far the cheapest and most feasible source known for the production of a practically pure potassium chloride in very large quantities.

But while the future of the potassium sulphate from alunite appears with almost a certainty to lie in fertilizers and in a minor degree as a raw material for the production of potassium carbonate, a pure potassium chloride from kelp would probably find quite different openings. Undoubtedly some of it would be utilized in fertilizers, but mainly it would be used in the production of potassium chlorate. Potassium chlorate is the basis for a type of "permissive" explosive much favored by construction engineers in the West and growing in favor everywhere. It is probable that a big impetus will be given to its use by the favor which it has found in the present war, but it is particularly as a necessary raw material in the production of safety matches that it is desired. This country could, and probably would, soon become the largest producer of safety matches with a satisfactory development of the kelp industry.

It seems desirable here to point out that, while there may be useful by-products from kelp developed some time in the future, there is no great promise of such in sight at the present time. The oft-heralded promise of cheap iodine is purely illusory. The main, practically the only, commercial source of iodine in the world today is the mother liquor from the crystallization of Chili saltpetre. But only about one-twelfth of the possible yield of iodine from this source is recovered in peace times, simply because the world's demands are thus fully satisfied, and the cost at which iodine can be produced in Chili would make it impracticable to recover it from the kelp, though there are no serious technical difficulties in so doing.

The *Macrocystis* has a life-history longer than one calendar year. It is probably a perennial. Moreover, harvesting it to a moderate depth appears to produce a stooling effect, causing it to grow more thickly and heavily. As the average length of a full-grown plant is about 100 feet, from 30 to 70 feet of the plant's length is streaming along near the surface with the tide or wind, and a cutting of four to six feet leaves no noticeable effect upon the harvested area. Consequently it seems probable that several cuttings a year can be made without damage to the bed. Indeed, observations on harvested areas indicate a decided improvement in growth is likely to ensue.

The beds all lie within the one marine league limit, hence control of them is vested in the State and not in the Federal Government. There appear to be no State laws applicable. Capital is notoriously timid of competition, and competition, even to the harvesting of the same bed by rival interests, is quite possible now, legally as well as physically. Moreover, however unfounded the fear may be, there has been a very real fear on the part of capital, in the absence of any pertinent laws, that it might become the victim of unfriendly legislation, and there has been a very real fear of the possibility of trouble from unscrupulous individual legislators. It has been the lack of adequate State legislation that has been, and is yet, the principal bar to the development of a potash-from-kelp industry.

Small amounts of dried kelp, kelp ash, and high-grade potassium chloride have been produced. One operator produced in all something over twenty tons of potassium chloride, but the company was improperly financed, was the victim of improper promoting and wildcat stock-jobbing, and was forced, because of its financial difficulties, to come to a stop just when it had demonstrated its ability to produce a high-grade product at a cost insuring a profit.

SUMMARY.

From the foregoing it appears that there are within the United States large stores of raw materials from which it is possible to obtain ample supplies of potash salts; that the technology of the subject is sufficiently developed to demonstrate the entire practicability of a supply from native sources, so far as physical factors are concerned. We can have "potash" if we really want it and are willing to pay for it. There are, however, serious commercial doubts affecting each of the four possible sources, and concerning the validity of these doubts opinions may well differ. Those most familiar with the problem are the most sanguine of the probability of commercial success.

While it is undoubtedly true that governmental efforts can yet furnish assistance, there is a very serious doubt as to how far these efforts should be continued. The time seems to have arrived when the commercial interests should themselves squarely assume the tasks confronting them and the costs of what further experimenting is necessary. This they have been slow to do, but there is rapidly accumulating evidence that these interests are responding to the spur of necessity, and that sooner or later potash salts from American sources are to be upon the market. An early cessation of the European war might delay but can no longer stop the development of our potash resources.

SOYA BEAN SITUATION IN SOUTH MANCHURIA.

The soya-bean crop of the Mukden district amounted to some 1,200,000 tons in 1913 and approximated 1,100,000 tons in 1914; of this production, 639,200 tons in 1913 and 603,548 tons in 1914 were transported by rail to South Manchurian seaports.

Of the beans exported, 150,000 tons went to Europe, 70,000 tons to Japan, and 80,000 tons to South China. Bean cake, the total production of which was 800,000 tons, was shipped mainly to Japan (500,000 tons) and South China (200,000 tons). Of the 70,000 tons of bean oil produced last year, 10,000 tons went to America, 10,000 tons to Europe, and 500 tons to Vladivostok, all being transshipped via Japan. Japan itself took 15,000 tons and South China 10,000 tons. Five firms, all Japanese, are engaged in the export business at present, other foreign firms having suspended trade in beans and bean products.

Since the war the exportation of all these products has been reduced, but local mills continue working at their full capacity. Baskets are still used for carrying oil from the producing centers to the railroad and for shipment to China coast ports; drums are used for consignments to America and Europe. About 240,000 tins and 120,000 wooden cases—mostly old cases from Shanghai—were imported during 1914.

THE LABORATORY

THE DETERMINATION OF ALKALINITY IN WATER.

By F. W. BRUCKMILLER.*

For the determination of alkalinity in waters the Standard Methods of Water Analysis recommends that a suitable portion of the water (usually 50 c.c.) be titrated with .02 N sulphuric acid using phenolphthalein and that a like portion be titrated with erythrosine of methyl orange. The results of each titration are expressed in p.p.m. of $CaCO^3$ and by means of the following table the alkalinity due to carbonates, hydrates, or bicarbonates is determined.

TABLE SHOWING RELATION BETWEEN ALKALINITY BY PHENOLPHTHALEIN AND THAT BY ERYTHROSINE IN PRESENCE OF BICARBONATES, CARBONATES AND HYDRATES.

	Bicarbonates	Carbonates	Hydrates
P=O	E	O	O
P ½E	E-2P	2P	O
P=½E	O	2P	O
P ½E	O	2(E-P)	2P-E
P=E	O	O	E

E=Erythrosine alkalinity.
P=Phenolphthalein alkalinity.

For practical routine work this method is not very well suited. Too much time is unnecessarily consumed in measuring out two separate portions of a water to determine its alkalinity, when the same results can be obtained by the use of only one. Furthermore, if both titrations are carried on in the same sample, the interpretation of the results are made a trifle confusing if one tries to use the above table. Because of these facts, the method given below, as well as the interpretation of the results, have been used exclusively by this laboratory and have been found to be quite satisfactory. We have been unable to find published elsewhere a similar statement of the procedure as we employ it. The subject matter it contains is not new, nor original with us. Cameron[1] first showed that carbonates could be titrated in the presence of bicarbonates, while Hehner[2] was the first to show that methyl orange could be used for the determination of bicarbonates. We have simply written down a long used procedure in a clear manner with the hope that it will prove of value to those who are now employed in water work as well as to those who will in the future take up such work.

PROCEDURE USING METHYL ORANGE.

To 50 c.c. (or to 100 c.c. if the alkalinity is low) of the water to be tested in a white porcelain casserole, or in an Erlenmeyer flask held over a white surface, add 4 drops of phenolphthalein indicator (1 gram in one liter of 95% alcohol). If the solution turns red, hydroxides or normal carbonates are indicated. Proceed then as in (a). If no change in color appears, proceed as in (b).

(a) Add N/50 sulphuric acid from a burette until the solution becomes colorless. Record the number of c.c. used and call phenolphthalein titration.

Now add 2 drops of methyl orange (.5 gram in one liter of water) indicator and add N/50 sulphuric acid until a faint pink occurs. Record the number of c.c. used, and call methyl orange titration.

(b) Add two drops of methyl orange if the phenolphthalein fails to turn the solution red, and then add N/50 sulphuric acid until a faint pink occurs. Record the number of c.c. used and call methyl orange titration.

PROCEDURE WITH ERYTHROSINE.

In place of methyl orange, erythrosine may be used. Using it the procedure is as follows:

To 50 c.c. (or 100 c.c. if alkalinity is low) of the water in a 250 c.c. glass stoppered bottle, add 4 drops of phenolphthalein indicator. If it turns red proceed as in (a) above down to where methyl orange is added. Then proceed as follows: Add 5 c.c. of neutral chloroform and 1 c.c. of erythrosine (.5 gram of sodium salt in one liter of distilled water). On shaking the solution becomes rose colored. Add acid until the solution becomes colorless. Record the number of c.c. used. This can be designated the "methyl orange titration" in conformity with the above, the erythrosine giving all that the methyl orange would.

If there is no phenolphthalein alkalinity proceed at once with erythrosine as indicated.

BICARBONATES.

The alkalinity is due to bicarbonates alone when phenolphthalein gives no coloration when added to the water. The number of c.c. of acid used with methyl orange x 20 (or 10 if 100 c.c. of water are used) gives parts per million $CaCO_3$ as bicarbonate alkalinity.

If the phenolphthalein titration is less than the methyl orange titration, carbonates and bicarbonates are present. The phenolphthalein titration gives half the carbonates according to the following equation:

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4$$

while the methyl orange titration gives all the bicarbonates already present in the water plus the bicarbonates formed from the carbonates during titration with phenolphthalein. The methyl orange titration minus the phenolphthalein titration multiplied by 20 (or 10 if 100 c.c. of water are used) gives parts per million bicarbonates in terms of calcium carbonate. The bicarbonate, carbondioxide as bicarbonate, and half bound carbondioxide are determined by the following factors:

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*Water and Sewage Laboratory, University of Kansas, Lawrence, Kan.

[1] Am. Chem. Jr., 1900, Vol. 23, page 481.

[2] Analyst, 8, 77.

Bicarbonate (HCO_3) 1.22 times the bicarbonate expressed in terms of calcium carbonate.

Carbonic acid (CO_2) as bicarbonate 0.88 times the bicarbonate expressed in terms of calcium carbonate.

Half bound carbonic acid (CO_2) 0.44 times the bicarbonate expressed in terms of calcium carbonate.

CARBONATES.

The alkalinity is due solely to normal carbonates when the phenolphthalein titration is equal to the methyl orange titration. The number of c.c. of N/50 sulphuric acid used with phenolphthalein multiplied by 40 (or by 20 when 100 c.c. of water are used) gives the parts per million of carbonates in terms of calcium carbonate. When the phenolphthalein titration is less than the methyl orange titration, bicarbonates and carbonates are present. The carbonate alkalinity expressed in parts per million of calcium carbonate is equal to the phenolphthalein titration multiplied by 40. When the phenolphthalein titration is greater than the methyl orange titration, carbonates and hydroxides are present. During the phenolphthalein titration the hydrates and half the carbonates are neutralized, while during the methyl orange titration the bicarbonates formed from the carbonates are neutralized. The methyl orange titration multiplied by 40 (or 20 when 100 c.c. of water are used) gives the carbonates in parts per million in terms of calcium carbonate. The carbonate, carbonic acid as carbonate and bound carbonic acid are determined from it by the following factors:

Carbonate (CO_3) 0.6 times the normal carbonates expressed in terms of calcium carbonate.

Carbonic acid as carbonate (CO_2) 0.44 times the normal carbonates expressed in terms of calcium carbonate.

Bound carbonic acid (CO_2) is the sum of the carbonic acid as carbonate plus one-half that as bicarbonate.

HYDROXIDES.

When hydroxides are present the phenolphthalein titration is greater than the methyl orange titration. If there is no methyl orange titration, the alkalinity is due solely to hydroxides. This is indicated when the solution turns pink upon the addition of methyl orange at the completion of the phenolphthalein titration. The number of c.c. N/50 H_2SO_4 used for phenolphthalein x 20 (or 10 if 100 c.c. of water are used) gives the hydroxides in parts per million in terms of $CaCO_3$. When phenolphthalein titration is greater, the number of c.c. used with phenolphthalein minus the c.c. used with methyl orange times 20 (or 10 when 100 c.c. of water are used) gives parts per million hydroxides in terms of $CaCO_3$.

The following table expresses the above in a more compact form and will no doubt prove useful.

TABLE SHOWING CALCULATION OF ALKALINITY FROM PHENOLPHTHALEIN AND MPTHYL ORANGE OR ERYTHROSINE TITRATION WHEN USING 50 C.C. OF WATER.

	Bicarbonates	Carbonates	Hydroxides
P*=O	20M	O	O
P M	20(M-P)	40P	O
P =M	O	40P	O
P M	O	40M	20(P-M)
M†=O	O	O	20M

(*) P=Penolphthalein titration.

(†) M=Methyl orange titration.

THERMAL REACTIONS OF AROMATIC HYDROCARBONS IN THE VAPOR PHASE.*

By W. F. RITTMAN, O. BYRON AND G. EGLOFF.

In connection with the phenomena of thermal decomposition or "cracking" of hydrocarbons a study has been outlined for the purpose of obtaining comprehensive data regarding the whole field. A first series of experiments[1] dealt with the production of gas and determined the influence of temperature, pressure and concentration on the yield and composition of the product. Another series of experiments[2] dealt with liquid reaction products and indicated conditions favorable for the production of (1) open-chain hydrocarbons and (2) aromatic hydrocarbons; it was shown that the temperature range may be divided roughly as follows with regard to the products of the cracking reaction; up to about 600° C. the formation of low-gravity hydrocarbons of the open chain class is favored; from 600° to 800° aromatic compounds are produced in large quantity; above 800° the maximum products are carbon and gas.

From both a scientific and a commercial point of view the differences among various aromatic hydrocarbons are of almost, if not quite, as great importance as the differences among classes. The present series of experiments has, therefore, been conducted for the purpose of establishing facts concerning the influence of conditions of temperature and pressure on inter-aromatic reactions. Four typical monocyclic hydrocarbons—cymene, xylene, toluene and benzene—were subjected to cracking, each at three different temperatures and at each temperature under four pressures. Some work has been done also with the solid hydrocarbons naphthalene and anthracene, but on account of experimental difficulties, the results obtained are only qualitative.

From the results of the study of reaction products, indications have been obtained which may be summarized in the following general way:

1—*(a)* The course of the reaction is in the direction of decrease in size of molecule when the degree of saturation is unchanged.

(b) Reactions may occur in the direction of

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*From The Journal of Industrial and Engineering Chemistry Published with the permission of the Director of the Bureau of Mines.

[1] Rittman and Whitaker, The Journal of Industrial and Engineering Chemistry, 6 (1914), 383 and 472.

[2] Rittman, Ibid., 7 (1915), 945.

de-hydrogenation either with increase or with decrease in size of molecule.

2—Reverse reactions occur in practically negligible amount.

HISTORICAL.

More or less work seems to have been done by previous investigators on the problem of thermal reactions of aromatic compounds but in no case has a systematic study been made. The information desired at present concerns the influence of conditions of temperature and pressure upon quantitative and qualitative relations among end products and this is not adequately supplied by the literature.

The classic researches of Bertholet[3] have furnished a foundation for our knowledge in this general field. His series of thermal reactions is comprehensive and the results obtained are valuable, though not such as to supply the needs of the present case.

Ferko[4] furnished some valuable information, particularly with regard to the direction of reactions. He passed the vapors of several hydrocarbons, either pure, or mixed with ethylene gas, through an iron tube heated over a 40 cm. length in a gas furnace. The products were condensed and their composition studied. The more important of the results obtained are summarized in Table I. Without attempting a detailed study of this table it may be seen that no reaction products are obtained which are not in the order of decrease of saturation, or of molecular weight if saturation remains unchanged. Thus benzene yields no toluene nor any other compound of equal saturation or of greater molecular weight. Naphthalene yields neither benzene nor toluene. From ethyl benzene, however, it is possible to obtain toluene, benzene and compounds of lower saturation. The work of Ferko seems to have been the most valuable of all hitherto done in this field but it gives little attention to the influence of temperature and none to that of pressure.

TABLE I.—SUMMARY OF RFSULTS OBTAINED BY FERKO.

Original Material Hydrocarbon.	Quantity. Grams.	Reaction Products. Percentages of Original Material. Benzene.	Toluene.	Styrolene.	Ethyl benzene.	Dinaphthalene.	Diphenyl.	Naphthalene.	Phenanthrene.	Anthracene.
Benzene and ethylene	1320	6.0	0.0	1.3	0.0	0.0	22.7	0.0	0.8	1.1
Toluene	1300	11.5	13.8	0.5	0.0	0.0	2.1	3.0	1.1	1.0
Toluene and ethylene	1300	15.4	12.3	0.8	0.0	0.0	0.0	0.0	0.0	1.5
Naphthalene and ethylene	900	0.0	0.0	0.0	0.0	13.3	0.0	44.5	0.1	0.0
Ethyl benzene	500	15.0	1.0	2.0	4.0	0.0	0.6	2.2	2.6	0.4

Haber[5] studied the thermal reactions of various substances, among them benzene, at temperatures ranging between 600-800° C. and 900-1000° C. One of his observations is contrary to the results of the present experiments. He states that although benzene goes readily to diphenyl it does not form naphthalene.

McKee[6] has, as a result of some qualitative experiments, concluded that the order of hydrocarbon decomposition is: higher paraffins→lower paraffins→olefins→acetylene→benzene and homologs→diphenyl→naphthalene, etc.,→tarry matter→carbon and gas. In his experiments benzene was passed through a hot copper tube and the degree of decomposition determined by change in specific gravity of the product. No analysis or separation seems to have been attempted upon the latter.

Smith and Lewcock[7] passed benzene through an iron tube at 800° C. obtained a 25 per cent yield of diphenyl. They were not, however, able to reverse the action, which inability they attributed to experimental difficulties. They observe that the quantity of diphenyl produced increased with the rate of feed, which indicates that this is not an equilibrium product, but simply one which is intermediate.

THEORETICAL.

GENERAL CONSIDERATIONS—In the present as well as in the earlier series of experiments cracking was produced in a system having a single (gaseous) phase. The characteristics and advantages of this method of procedure have been already discussed in detail.[8] It is sufficient in the present connection to recall the

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[3] Ann. chim. phys., [4] 9 (1866), 445; 12 (1867), 5; (1869), 143.
[4] Ber., 20 (1887), 660.

TABLE II.—QUANTITATIVE STUDY OF EQUILIBRIA.

No.	Reactions.	Heats of reaction.	Volume changes.	(Formulas refer to partial pressures).	Approximate. K_{650}	K_{725}	K_{800}
1	$4C_{10}H_{14} \rightleftarrows 5C_8H_{10} + 3H_2$ .... Cymene Xylene	—18000	4 to 8	$K = \frac{(C_8H_{10})^5(H_2)^3}{(C_{10}H_{14})^4}$	6.8 × 10^{32}	4.7 × 10^{32}	4.7 × 10^{32}
2	$7C_{10}H_{11} \rightleftarrows 10C_7H_8 + 9H_2$ .... Cymene Toluene	—82000	7 to 19	$K = \frac{(C_7H_8)_{10}(H_2)^9}{(C_{10}H_{14})^7}$	2.0 × 10^{66}	1.4 × 10^{68}	2.0 × 10^{70}
3	$3C_{10}H_{14} \rightleftarrows 5C_6H_6 + 6H_2$ .... Cymene Benzene	—68500	3 to 11	$K = \frac{(C_6H_6)^5(H_2)^6}{(C_{10}H_{14})^3}$	7.8 × 10^{40}	2.8 × 10^{42}	1.0 × 10^{44}
4	$7C_8H_{10} \rightleftarrows 8C_7H_8 + 3H_2$ .... Xylene Toluene	—90800	7 to 11	$K = \frac{(C_7H_8)^8(H_2)^3}{(C_8H_{10})^7}$	1.1 × 10	6.6 × 10^8	3.1 × 10^{10}
5	$3C_8H_{10} \rightleftarrows 4C_6H_6 + 3H_2$ .... Xylene Benzene	—65600	3 to 7	$K = \frac{(C_6H_6)^4(H_2)^3}{(C_8H_{10})^3}$	1.1 × 10^{13}	2.1 × 10^{14}	4.3 × 10^{15}
6	$6C_7H_8 \rightleftarrows 7C_6H_6 + 3H_2$ .... Toluene Benzene	—40700	6 to 10	$K = \frac{(C_6H_6)^7(H_2)^3}{(C_7H_8)^6}$	2.9 × 10^{17}	3.2 × 10^{18}	2.7 × 10^{19}

fact that the basic reason for the employment of the one-phase system is that it permits the independent regulation of the two factors of temperature and pressure. In any two-phase system each of these is a function of the other. There are numerous other advantages but these have received adequate discussion in earlier connections.

EQUILIBRIUM RELATIONS—In each of the two preceding communications applications have been given of the Nernst approximation formula for equilibrium constants. The use of this expression is particularly helpful in connection with the present series of experiments as the reactions are obtained upon pure chemical compounds instead of complex mixtures. It is possible, therefore, to write equations which are entirely representative of what may occur instead of merely typical. The figures obtained are understood to be representative only of general tendencies but are of much value when interpreted in this light.

The figures in Table II represent equilibrium relations for a series of reactions, any or all of which may have occurred in the present experiments. A first point to be considered is the influence of variations in pressure. All the reactions occur with an increase in volume and therefore it is to be expected that the effect of pressure will be inimical. This consideration is, however, complicated by the necessity of taking account of another factor. The use of the Nernst formula assumes that the reactions have proceeded until equilibrium has been reached and it is doubtful if this is the case, especially for the reactions at lower temperatures.[9] According to the law of mass action, reaction velocity is proportional to the product of the concentrations of the reacting substances and concentration is, in the present case, directly proportional to pressure. It appears, therefore, that increase in pressure may be favorable up to a point where the reactions proceed with sufficient rapidity to attain to a state of equilibrium. Increase in pressure above this will undoubtedly tend to shift the equilibrium unfavorably for the reactions indicated from left to right in the equations.

Consideration of the effect of temperature is also complicated. The constants invariably increase with temperature and this should indicate that even greater degrees of heat would be favorable. It must be remembered, however, that no one reaction can be considered as happening alone. Each major reaction is coincident with a number of by-reactions and the establishment of conditions which apparently are favorable for the main reaction may in actual fact hinder it on account of greater favoring of minor reactions; for example, benzene formation would seem to be favored by increasing temperature even beyond the 800° limit. It appears, however, that even at this mark the reaction has suffered on account of greater favoring of other products and the maximum yields of benzene occur in the 650° and 725° runs.

The chief value of the constants lies in the indication they give of the general tendencies of reactions. An examination of the values in Table II makes evident the fact that all the reactions should occur principally in the direction indicated from left to right in the equations. The magnitude of the reverse reactions would be proportional to the reciprocals of the constants and these in most cases are negligibly small.

EXPERIMENTAL.

The scheme of procedure followed in the present experiments was, with slight exceptions, identical with that described in the earlier communications.[10] The apparatus consisted of an electrically heated cracking furnace equipped at one end with an oil-feed cup and a vaporizing device, and at the other with a condenser, receivers for liquid reaction products, and a pressure regulating device.

One modification in the making of the "run" is worthy of mention. In the earlier series of experiments pressures were built up in the cracking furnace by the decomposition of some of the oil used in the run. This necessitated the introduction of a source of error, which in the more recent experiments it has been found possible to eliminate. Before the beginning of each pressure run the system was connected with a compressor and natural gas[11] pumped in until the gauge gave the proper reading. The compressor was then shut off by closing a valve and the run started.

For all the liquid hydrocarbons the original material was allowed to flow into the furnace at the rate of about 6 cc. per minute. In the cases when the solid hydrocarbons, naphthalene and anthracene, were used as starting-out material it was, of course, necessary to keep them in a molten condition during the run by applying heat to the feed cup. Even then considerable experimental difficulty was involved and no attempt was made to obtain results of more than qualitative accuracy.

The supplementary determinations were made upon quantities of recovered oil too small to permit separation of pure products. A single analytical distillation was made through an 8-in. Hempel column and cuts made at 100°, 125°, 150° and 200°. The first cut was taken as representative of benzene, the second of toluene, the third of xylene, and the fourth of cymene. Above 200° the distillation was continued with a shorter fractionating column and cuts made at intervals of 50°. These distillates were chilled and examined for the separation of solid naphthalene and

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[5] Ber., 29 (1896), 2691.

[6] Jour. Soc. Chem. Ind., 27 (1904), 403.

[7] Jour. Chem. Soc., 101 (1912), 1453.

[8] Rittman, Loc. cit.

[9] Rittman, The Journal of Industrial and Engineering Industry, 6 (1914), 1027; Jour. Soc. Chem. Ind., 33 (1914), 626; Whitaker and Alexander, The Journal of Industrial and Engineering Chemistry, 7 (1915), 481.

[10] Whitaker and Rittman, Loc. cit.; Rittman, Loc. cit.

[11] Natural gas was used because it is largely methane, which is one of the end products of all cracking reactions.

anthracene. On account of the smallness of the quantities obtained no attempt was made to obtain quantitative results for the solid products.

The total scheme of procedure may be summarized as follows:

"RUN" OR MAJOR EXPERIMENT.

1—Cracking of a quantity (generally 500-600 cc.) of hydrocarbon under regulated conditions of temperature and pressure.

2—Determination of quantities of liquid and solid reaction products.

SUPPLEMENTARY DETERMINATIONS.

1—Distillation of liquid reaction products through Hempel fractionating columns.

2—Determinations of specific gravities of total reaction products and of distillation cuts.

EXPERIMENTAL MATERIAL.

Benzene was the purest material commercially obtainable. The sample used was particularly good as is shown by the data in Table III. Toluene and xylene were the "chemically pure" market products. Cymene also was a commercial product.

TABLE III.—ORIGINAL PRODUCTS USED IN EXPERIMENTS

Product.	Sp. gr. 15°/15°	Fractional Distillation.				
Benzene	0.879	98 per cent between 80 and 81° C.				
Toluene	0.869	Temp.	98	98-100	100-110	110-115° C.
		%	1st drop	0.2	92.0	4.0
Xylene	0.862	Temp.	88	88-120	120-137° C.	
		%	1st drop	0.7	99.3 (flask dry)	
Cymene	0.863	Temp.	165°	170-179° C.		
		%	1st drop	90.0		

GENERAL USES AND EXPERIMENTS.

The entire collection of data obtained in the present series of experiments appears in Table IV. This table is, on account of its size and necessity arrangement, not particularly readable and special tables have been prepared to set forth the various indications obtained: it does, however, show the scope and magnitude of the work and indicates the nature of the measurements which have been made.

Results are recorded in terms of percentage by volume except in cases where either starting-out material or reaction product was a solid. In such instances mass relations are given.

It will be noted that for the four liquid hydrocarbons—cymene, xylene, toluene and benzene—the series of experiments are complete. Quantitative reresults for the distillations are given for cuts up to 200° and above that temperature the indications for naphthalene and anthracene are given by plus (+) and minus (—) signs. For the experiments where naphthalene and anthracene were starting-out material no distillates were obtained below 200° C. and all the results are therefore qualitative.

ANALYSES OF QUANTITATIVE RESULTS (TABLE V).

(a) Percentage yield of liquid reaction products decreases with increase in temperature and in general with increase in pressure. This percentage represents the total of liquid products and soluble products which are soluble therein, excluding only carbon and gas. The figures given are in a way representative of the stability of the various compounds, their resistance to conversion into carbon and gas being indicated by the amount of liquid product obtained. It appears that for the four liquid hydrocarbons, the order of decreasing stability is benzene, toluene, xylene and cymene. This is as would be expected on the grounds of the theory that with similar molecular form the more unwieldy units of matter are the more easily broken down.

(b) PERCENTAGE OF ORIGINAL HYDROCARBON RECOVERED is another index of the stability of the compounds cracked. It represents total resistance to transformation while the percentage yield of liquid products represents resistance to conversion into carbon and gas. It appears that the order of stability is the same as that indicated in *(a)* but that there are greater differences. The effects of temperature and pressure are analogous to those indicated in *(a)*.

(c) BENZENE FORMATION—It appears from the figures in Table V*c* that benzene is formed in appreciable quantity from each of the three hydrocarbons, cymene, xylene, and toluene. The figures in Table IV indicate that neither benzene nor any of the other three monocyclic compounds are produced by the cracking of naphthalene or anthracene.

Section B of Table V*c* shows that optimum conditions for benzene formation are represented by the temperatures 650° and 725° and that pressure is favorable up to a certain limit which appears to be somewhere between 1 and 12 atmospheres. The runs at 18 atmospheres in general show decreases in the amount of benzene produced. This seems to indicate that somewhere between the pressures of 1 and 12 atmospheres a sufficient concentration is attained to permit the hydrocarbons to reach a state of equilibrium during their passage through the furnace and that the higher pressures are unfavorable for benzene production, as is indicated by the volume changes occurring in the reactions.

(d) TOLUENE FORMATION—Toluene may be formed from both xylene and cymene, most readily from the former. The amount which can be produced from benzene is negligible, that from naphthalene and anthracene nil. The effects of temperature and pressure seem rather irregular, very possibly on account of experimental error. The general tendency seems to be for maximum yields to occur with decreasing temperature as pressure increases. Thus in the xylene figures in Section B, Table V*d*, a maximum appears at 800° for vacuum runs, at 725° for runs at 1 atmosphere and at 650 for the runs at 12 atmospheres. Beyond this point the curve seems to swing the other way. A like tendency will be noted among cymene figures if the obviously wrong bracketed value is omitted from consideration.

(e) XYLENE FORMATION—The figures in Table V*c* show that while xylene may be formed in moderate quantity from cymene, the amounts produced from

toluene and benzene are exceedingly small. The formation of xylene seems to be favored by low temperature and low pressure.

(f) CYMENE FORMATION—Cymene is formed in negligible quantity from xylene, toluene and benzene (Table V*f*), and not at all from naphthalene and anthracene. This compound appears to be particularly unstable under conditions included in the present experiments, as is evidenced by the fact that only a small amount (13.0 per cent on the average) remains unchanged when this hydrocarbon is employed as starting-out material.

TABLE IV.—GENERAL RESULT OF CRACKING EXPERIMENTS.

Temperatures (°C.)	650		650		650		650		725		725		725		725	
	Vac.		1 At.		12 At.		18 At.		Vac.		1 At.		12 At.		18 At.	
Cymene—																
Volume used, cc.	500		600		600		600		500		400		600		600	
Per cent vol. recovered	83.0		62.0		53.3		40.8		52.0		40.0		27.5		25.0	
Per cent wt. carbon	1.8		1.0		10.2		16.3		2.4		3.6		37.4		32.8	
Specific gravity	0.895		0.921		0.924		0.916		0.927		0.982		0.945		0.934	
First drop	97°		69°		80°		70°		97°		...		75°		...	
	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
0-100°	0.2	.....	9.2	0.877	12.0	0.876	15.1	0.875	0.2	....	3.7	....	10.2	0.881	3.8	0.872
100-125°	14.5	0.869	2.5	0.874	2.7	0.875	1.9	0.873	3.9	0.878	7.4	0.876	2.3	0.870	5.0	0.877
125-150°	17.8	0.872	5.9	0.876	4.0	0.874	4.9	0.876	8.9	0.880	5.2	0.885	2.1	0.870	2.8	....
150-200°	34.5	0.878	21.6	0.899	21.3	0.874	10.6	0.873	17.0	0.888	5.4	0.898	3.0	0.898	7.5	0.870
Naphthalene	—	.....	—	.....	+	.....	+	.....	—	....	+	....	+	....	—	....
Anthracene	—	.....	—	.....	—	.....	+	.....	—	....	—	....	—	....	—	....
Xylene—																
Volume used, cc.	500		500		600		600		500		500		600		600	
Per cent vol. recovered	95.0		69.0		66.0		64.3		72.0		60.0		54.2		46.6	
Per cent wt. carbon	0.9		1.5		....		4.4		6.0		—		13.6		25.8	
Specific gravity	0.879		0.905		0.914		0.899		0.888		0.906		0.911		0.900	
First drop	77°		80°		60°		...		68°		82°		65°		98°	
	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
0-100°	0.3	.....	4.1	0.868	3.8	0.855	0.6	.....	0.0	....	2.0	....	3.2	0.857	0.0	....
100-125°	2.6	.....	15.4	0.870	18.7	0.867	9.2	0.858	9.2	0.861	34.5	0.862	15.2	0.869	12.6	0.872
125-150°	80.0	0.868	37.7	0.870	31.7	0.868	45.0	0.856	52.5	0.862	40.0	0.877	27.0	0.862	26.0	0.869
150-200°	1.9	.....	2.2	0.911	0.7	.....	0.6	.....	2.4	....	6.0	0.899	0.0	....	1.6	....
Naphthalene	—	.....	—	.....	—	.....	+	.....	—	....	+	....	—	....	+	....
Anthracene	—	.....	—	.....	—	.....	—	.....	—	....	+	....	—	....	—	....
Toluene—																
Volume used, cc.	500		600		480		600		500		600		600		475	
Per cent vol. recovered	98.0		98.3		94.8		60.8		85.0		64.2		48.3		18.0	
Per cent wt. carbon	0.0		1.0		4.7		5.9		1.4		1.3		20.1		34.0	
Specific gravity	0.872		0.894		0.933		0.912		...		0.924		0.918		0.929	
First drop	...		66°		88°		82°		80°		76°		...		73°	
	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
0-100°	0.0	.....	3.9	.....	21.8	0.872	18.2	0.877	2.1	....	17.3	0.874	30.7	0.883	10.4	0.879
100-125°	91.6	0.871	85.0	0.875	55.0	0.868	31.0	0.874	70.5	0.870	34.0	0.873	7.5	0.870	2.7	....
125-150°	3.4	.....	0.2	.....	0.0	.....	0.0	.....	4.2	....	0.0	....	0.7	....	0.0	....
150-200°	....	.....	0.5	.....	0.0	.....	0.0	.....	0.2	....	2.6	....	1.2	....	5.0	....
Naphthalene	+	.....	+	.....	—	.....	+	.....	+	....	+	....	+	....	—	....
Anthracene	—	.....	—	.....	—	.....	—	.....	—	....	—	....	+	....	—	....
Benzene—																
Volume used, cc.	500		600		600		335		500		500		600		600	
Per cent vol. recovered	90.0		86.6		87.5		73.1		94.0		90.0		58.3		53.3	
Per cent wt. carbon	0.2		0.9		1.5		11.9		1.0		1.4		15.3		34.0	
Specific gravity	0.896		0.898		0.941		0.921		0.904		0.945		0.946		0.923	
First drop	64°		69°		69°		76°		76°		65°		70°		71°	
	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
0-100°	78.5	0.881	66.5	0.885	59.4	0.886	57.0	0.878	77.5	0.888	61.5	0.815	39.7	0.886	42.3	0.885
100-125°	1.6	0.882	0.0	.....	0.1	.....	0.4	.....	1.4	....	0.9	....	0.0	....	0.0	....
125-150°	0.8	.....	0.0	.....	0.0	.....	0.0	.....	1.4	0.864	0.7	....	0.0	....	0.0	....
150-200°	0.4	.....	1.2	.....	0.0	.....	0.0	.....	2.8	0.906	0.7	....	0.0	....	0.0	....
Naphthalene	+	.....	+	.....	+	.....	+	.....	+	....	—	....	+	....	+	....
Anthracene	+	.....	—	.....	—	.....	—	.....	—	....	—	....	+	....	+	....
Naphthalene—																
Weight used, grams	400		400		432		...		400		414		384		...	
Per cent vol. recovered	76.0		65.7		30.0		...		66.4		65.4		...		...	
Per cent carbon	0.0		3.3		21.0		...		3.5		7.0		40.0		...	
First drop	205°		200°		205°		...		200°		210°		...		...	
Naphthalene	+		+		+		...		+		+		+		...	
Anthracene	—		—		—		...		+		+		+		...	
Anthracene—	...				...		...									
Weight used, grams	...		125		...		...		125		...		...		...	
Per cent recovered	...		63.2		...		...		56.0		...		...		...	
Per cent carbon	...		18.0		...		...		22.0		...		...		...	
First drop	...		300°		...		...		...		...		...		...	
Naphthalene	...		—		...		...		—		...		...		...	
Anthracene	...		+		...		...		+		...		...		...	

ANALYSIS OF QUALITATIVE RESULTS (TABLE VI).

NAPHTHALENE FORMATION—The qualitative indications of Table VI point out the fact that naphthalene is generally one of the products of the cracking of the monocyclic compounds: cymene, xylene, toluene and benzene. This is in part contrary to the observation of Haber[12] who states that while diphenyl may be produced by the thermal decomposition of benzene, naphthalene is not so formed. Diphenyl was undoubtedly produced in the present experiments, although no attempt was made to isolate or identify it. Direct evidence was obtained of the formation of naphthalene and in some cases, notably in the benzene series, it appeared in considerable quantity in the cooled distillates.

800		800		800		800	
Vac.		1 At.		12 At.		18 At.	
500		500		600		600	
49.0		17.6		15.8		0.0	
1.3		9.0		20.8		0.0	
0.951		0.995		0.926		...	
73°		...		...		...	
% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
1.5	....	1.6	0.872	3.8	0.865	0.0	....
4.7	0.874	1.9	0.874	1.3	0.868	0.0	....
9.5	0.882	1.6	0.878	1.6	....	0.0	....
14.5	0.895	1.6	....	5.7	0.880	0.0	....
—	....	—	....	—	....	—	....
—	.	—	....	—	....	—	....

500		590		600		425	
66.0		27.1		31.7		11.5	
0.5		25.0		39.5		38.4	
0.912		0.923		0.904		0.945	
87°		77°		68°		...	
% Orig.	Sp. Gr.	% Orig	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
0.7	....	8.3	0.878	9.1	0.866	5.4	0.875
18.5	0.874	7.2	0.874	8.6	0.867	0.8	0.875
35.6	0.872	4.5	0.874	7.9	0.864	1.1	0.875
2.3	....	0.9	....	...	....	1.5	0.875
—	....	—	....	—	....	—	....
+	....	—	....	—	....	—	....

500		600		600		600	
66.0		32.5		34.2		11.7	
1.8		40.0		24.3		23.4	
0.903		0.931		0.925		0.927	
		...		...		...	
% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
5.6	....	17.6	0.880	16.4	0.866	3.0	0.874
49.5	0.872	6.6	0.879	7.5	0.873	4.0	0.874
0.0	....	0.0	....	1.2	....	1.6	....
0.1	....	0.0	....	0.0	....	0.7	....
+	....	—	....	+	....	—	....
+	...	—	....	+	....	—	....

500		500		600		600	
87.0		62.0		22.5		18.3	
2.5		1.6		6.3		35.0	
0.906		0.959		0.922		0.928	
77°		76°		68°		64°	
% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.	% Orig.	Sp. Gr.
63.0	0.883	35.6	0.886	16.1	0.888	12.1	0.884
0.9	....	0.3	....	0.0	....	0.0	....
1.7	....	0.5	....	0.0	....	0.0	....
6.9	...	3.0	....	0.0	....	0.0	....
+	....	+	....	+	....	+	....
—	....	—	....	—	....	—	....

400	500	427	...
85.9	80.8	19.8	...
9.5	13.6	5.0	...
...	...	...	...
+	+	+	...
+	+	+	...
...	...	...	...
...	...	...	...
...	...	...	...
...	...	...	...
...	...	...	...
...	...	...	...

TABLE VI—ANALYSIS OF QUALITATIVE RESULTS.

Temp. °C.	Press. Atm.	Naphthalene Formation				Anthracene Formation				
		Cymene	Xylene	Toluene	Benzene	Cymene	Xylene	Toluene	Benzene	Naphthalene
650	Vac.	+	—	+	+	—	—	—	+	—
	1	—	—	+	+	—	—	—	—	—
	12	+	—	—	+	—	—	—	—	—
	18	+	+	+	+	+	—	—	—	
725	Vac.	—	—	+	+	—	—	—	—	+
	1	+	+	+	—	—	+	—	—	+
	12	+	—	+	+	—	—	+	+	+
	18	—	+	—	+	—	—	—	+	
800	Vac.	—	—	+	+	—	+	+	—	+
	1	—	—	—	+	—	—	—	—	+
	12	—	—	+	+	—	—	+	—	+
	18	—	—	—	+	—	—	—	—	

ANTHRACENE FORMATION—The indications of anthracene formation are not particularly satisfactory except that they establish the fact that anthracene may be formed by the heating of the other hydrocarbons. Anthracene is formed with some readiness by the cracking of naphthalene and it occasionally appears in the higher distillation cuts from the runs with liquid hydrocarbons.

SUMMARY.

It will be noted from the results of the present experiments that from cymene it is possible to produce by "cracking" all the other hydrocarbons of the series, such as xylene, toluene, benzene, naphthalene and anthracene. From xylene results toluene, benzene, naphthalene, and anthracene but no cymene. Toluene yields benzene, naphthalene and anthracene, but no cymene and no xylene. Benzene goes to naphthelene and anthracene but not to any of its higher homologs. From naphthalene, anthracene is readily obtainable but none of the monocyclic hydrocarbons, benzene, toluene, xylene and cymene, are produced. Anthracene yields no naphthalene but goes to tarry matter, carbon and gas. These relations can be rendered clearer by the following scheme:

C_9H_{12}—C_8H_{10}, C_7H_8, C_6H_6, $C_{10}H_8$, $C_{14}H_{10}$
CYMENE—Xylene, Toluene, Benzene, Naphthalene, Anthracene
XYLENE—Toluene, Benzene, Naphthalene, Anthracene (No *Cymene*)
TOLUENE—Benzene, Naphthalene, Anthracene (No *Cymene, Xylene*)
BENZENE—Naphthalene, Anthracene (No *Cymene, Xylene, Toluene*)
NAPHTHALENE—Anthracene (No *Cymene, Xylene, Toluene, Benzene*)
ANTHRACENE—Tarry Matter, Carbon and Gas (No *Naphthalene, etc.*)

Other compounds such as diphenyl, methyl naphthalenes and anthracenes, phenanthrene, etc., are undoubtedly formed but in the absence of identification they have been omitted from mention in the present connection.

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[12] Loc. cit.

TABLE V—ANALYSIS OF QUANTITATIVE RESULTS.

		(a) Yield (%) of Liquid Reaction Products.				(b) Recovery (%) of Original Hydrocarbon.				Percentage Formation of Liq (c) Benzene Formation.				(d) Toluene Formation.			
Section A: Temp. ° C.	Press. Atm.	Cymene	Xylene	Toluene	Benzene	Cymene	Xylene	Toluene	Benzene	Cymene	Xylene	Toluene	Benzene	Cymene	Xylene	Toluene	Benzene
650	Vac.	83.0	95.0	98.0	90.0	34.5	80.0	91.6	78.5	0.2	0.3	6.0	78.5	[14.5]	2.6	91.6	1.6
	1	62.0	69.0	98.3	86.6	21.6	37.7	85.0	66.5	9.2	4.1	3.9	66.5	2.5	15.4	85.0	0.0
	12	53.3	66.0	94.8	87.5	21.3	31.7	55.0	59.4	12.0	3.8	21.8	59.4	2.7	18.7	55.0	9.1
	18	40.8	64.3	60.8	73.1	10.6	45.0	31.0	57.0	15.1	0.6	18.3	57.0	1.9	9.2	31.0	0.5
725	Vac.	52.0	72.0	85.0	94.0	17.0	52.5	70.5	77.5	0.2	0.0	2.1	77.5	3.9	9.2	70.5	1.4
	1	40.0	60.0	64.2	90.0	5.4	40.0	34.0	61.5	3.7	2.0	17.3	61.5	7.1	34.5	34.0	0.9
	12	27.5	54.2	48.3	58.3	3.0	27.0	7.5	39.7	10.2	3.2	30.7	39.7	2.3	15.2	7.5	0.0
	18	25.0	46.6	18.0	53.3	7.5	26.0	2.7	42.3	3.8	0.0	10.4	42.3	5.0	12.6	2.7	0.0
800	Vac.	49.0	66.0	66.0	87.0	14.5	35.6	49.5	63.0	1.5	0.7	5.6	63.0	1.7	18.5	49.5	1.0
	1	17.6	27.1	32.5	62.0	1.6	4.5	6.6	35.6	1.6	8.3	17.6	35.6	1.9	7.2	6.6	0.5
	12	15.8	31.7	31.2	22.5	5.7	7.9	7.5	16.1	3.8	9.1	16.4	16.1	1.3	8.6	7.5	0.0
	18	0.0	11.5	11.7	18.3	0.0	1.1	4.0	12.1	0.0	5.1	3.0	12.1	0.0	0.8	4.0	0.0
Average		38.8	54.2	59.3	65.5	11.9	30.6	37.1	50.7	5.1	3.1	12.3	50.7	1.0	11.1	37.1	0.5

Section B: Hydrocarbon	Temp. ° C.	(a) Vac	(a) 1 Atm.	(a) 12 Atm.	(a) 18 Atm.	(b) Vac.	(b) 1 Atm.	(b) 12 Atm.	(b) 18 Atm.	(c) Vac.	(c) 1 Atm.	(c) 12 Atm.	(c) 18 Atm.	(d) Vac.	(d) 1 Atm.	(d) 12 Atm.	(d) 18 Atm.
Cymene	650	83.0	62.0	53.3	40.8	34.5	21.6	21.3	10.6	0.2	9.2	12.0	15.1	[14.5]	2.5	2.7	1.9
	725	52.0	40.0	27.5	25.0	17.0	5.4	3.0	7.5	0.2	3.7	10.2	3.8	3.9	7.4	2.3	5.0
	800	49.0	17.6	15.8	0.0	14.5	1.6	5.7	0.0	1.5	1.6	3.8	0.0	4.7	1.9	1.3	0.0
Xylene	650	95.0	69.0	66.0	64.3	80.0	37.7	31.7	45.0	0.3	4.1	3.8	0.6	2.6	15.4	18.7	9.2
	725	72.0	60.0	54.2	46.6	52.5	40.0	27.0	26.0	0.0	2.0	3.2	0.0	9.2	31.5	15.2	12.6
	800	66.0	27.1	31.7	11.5	35.6	4.5	7.9	1.1	0.7	8.3	9.1	5.4	18.5	7.2	8.6	0.8
Toluene	650	98.0	98.3	94.8	60.8	91.6	85.0	55.0	31.0	0.0	3.9	21.8	18.3	91.6	85.0	55.0	31.0
	725	85.0	64.2	48.3	18.0	70.5	34.0	7.5	2.7	2.1	17.3	30.7	10.4	70.5	34.0	7.5	2.7
	800	66.0	32.5	34.2	11.7	49.5	6.6	7.5	4.0	5.6	17.6	16.4	3.0	49.5	6.6	7.5	4.0
Benzene	650	90.0	86.6	87.5	73.1	78.5	66.5	59.4	57.0	78.5	66.5	59.4	57.0	1.6	0.0	0.1	0.5
	725	94.0	90.0	58.3	53.3	77.5	61.5	39.7	42.3	77.5	61.5	49.7	42.3	1.4	0.9	0.0	0.0
	800	87.0	62.0	22.5	18.3	63.0	35.6	16.1	12.1	63.0	35.6	16.1	12.1	1.0	0.5	0.0	0.0

On the basis of the evidence at hand it seems justifiable to state that the course of the cracking reaction in the aromatic series may be indicated as follows and that reverse action occurs in practically negligible amount: Higher benzene homologs → lower benzene homolog → benzene → (diphenyl) → naphthalene → anthracene → carbon and gas.

RUBBER TRADE OF EAST INDIES AND THE STRAITS.

The U. S. Consul, B. S. Rairden, Batavia, Java, reports that the United States bought 36 times as much plantation rubber from Java in the first half of 1915 as in the corresponding 6 months of 1914, and became this island's best customer. The Netherlands took only a little more than half as much and fell to third place; while Great Britain occupied second place in both semesters, as Table I shows:

TABLE I.

Exported to—	January-June, 1914. Ficus. Pounds.	Hevea. Pounds.	Ceara. Pounds.	Total.* Pounds.
United States	......	88,389	....	88,389
Netherlands	30,652	1,849,054	111,325	2,026,306
Great Britain	38,203	1,730,848	26,771	1,815,345
Germany	......	60,830	......	63,565
Belgium	462	406,520	....	406,982
Other parts of Europe	......	6,811	....	6,811
Straits Settlements	328	114,138	260	114,726
Australia	......	....	....	......
Other countries	......	.... .	. . . .	. . ..
Total	69,045	4,256,590	141,359	4,522,124

Exported to—	January-June, 1915. Ficus. Pounds.	Hevea. Pounds.	Ceara. Pounds.	Total.* Pounds.
United States	......	3,160,676	8,692	3,169,368
Netherlands	22,359	979,902	11,048	1,015,597
Great Britain	12,705	2,166,879	9,788	2,245,562
Germany	......	....	....	....
Belgium	......	....	....	....
Other parts of Europe	......	....	......	....
Straits Settlements	9,299	294,897	....	304,196
Australia	......	86,625	......	86,625
Other countries	433	194,762	....	195,195
Total	44,796	6,883,741	29,528	7,016,543

Exports of plantation rubber from Belawan, Deli (Sumatra East Coast) in the first half of the current year amounted to 5,584,777 lbs., a figure 75 per cent in excess of the total for the corresponding months of 1914. Of this gain 1,117,659 lbs. can be credited to the United States, as that country made no purchases from the East Coast during January-June, 1914; Great Britain took 2,738,600 lbs. more, and the Netherlands 13,308 lbs. more. Offsetting these increases were declines totaling 1,472,093 lbs., so that the net gain for the half-year was 2,397,474 lbs. The distribution of these cargoes was:

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*Includes Castilloa rubber not shown to the extent of 55,130 pounds (32,875 pounds to the Netherlands, 19,520 to Great Britain, and 2,735 to Germany) in the first half of 1914 and 58,478 pounds (2,288 pounds to the Netherlands and 56,190 to Great Britain) in January-June, 1915.

uid Aromatic Hydrocarbons.

(*e*) Xylene Formation.				(*f*) Cymene Formation.			
Cymene	Xylene	Toluene	Benzene	Cymene	Xylene	Toluene	Benzene
17.8	80.0	3.4	0.8	34.5	1.9	0.0	0.4
5.9	37.7	0.0	0.0	21.6	2.2	0.5	1.0
4.0	31.7	0.0	0.0	21.3	0.7	0.0	0.0
4.9	45.0	0.0	0.0	10.6	0.6	0.0	0.0
8.9	52.5	4.2	1.4	17.0	2.4	0.2	2.8
5.2	40.0	0.0	0.7	5.4	6.0	1.6	0.7
2.1	27.0	0.7	0.0	3.0	0.0	1.2	0.0
2.8	26.0	0.0	0.0	7.5	0.0	0.9	0.0
9.5	35.6	0.0	1.7	14.5	2.3	0.1	6.9
1.6	4.5	0.0	0.5	1.6	0.9	0.0	3.6
1.6	7.9	1.2	0.0	5.7	0.0	0.0	0.0
0.0	1.1	1.6	0.0	0.0	1.5	6.7	0.0
5.4	30.6	0.9	0.4	11.9	1.2	0.9	1.2
	1	12	18		1	12	18
Vac.	Atm.	Atm.	Atm.	Vac.	Atm.	Atm.	Atm.
17.8	5.9	4.0	4.9	34.5	21.6	21.3	10.6
8.9	5.2	2.1	2.8	17.0	5.4	3.0	7.5
9.5	1.6	1.6	0.0	14.5	1.6	5.7	0.0
80.0	37.7	31.7	45.0	1.9	2.2	0.7	0.6
52.5	40.0	27.0	26.0	2.4	6.0	0.0	0.0
35.6	4.5	7.9	1.1	2.3	0.9	0.0	1.5
3.4	0.0	0.0	0.0	0.0	0.5	0.0	0.0
4.2	0.0	0.7	0.0	0.2	1.6	1.2	0.9
0.0	0.0	1.2	1.6	0.1	0.0	0.0	6.7
0.8	0.0	0.0	0.0	0.4	1.0	0.0	0.0
1.4	0.7	0.0	0.0	2.8	0.7	0.0	0.0
1.7	0.5	0.0	0.0	6.9	3.0	0.0	0.0

Exported to—	1914. Pounds.	1915. Pounds.
United States	....	1,117,659
Netherlands	667,335	680,643
Great Britain	699,571	3,138,171
Belgium	10,868	....
Germany	9,733	....
Straits Settlements	1,799,796	348,304
Total	3,187,303	5,584,777

The figures presented in Table 11 have been taken from the official returns of the respective countries and represent the total exports during the calendar years named. The quantities are stated in hundredweights of 112 pounds for Ceylon, kilos of 2.2046 pounds for the Dutch East Indies, and piculs of 133.33 pounds for the Straits Settlements; the values in rupees, equivalent to 32.443 cents U. S. gold; in guilders, equivalent to 40.2 cents; and in Straits Settlements dollars, equivalent to 56.78 cents.

TABLE I .

	Quantity.	Value.
CEYLON.		
Rubber exported in—	Cuts.	Rupees.
1911	61.212	28,356,056
1912	132,569	52,178,051
1913	226,491	61,269,262
1914	306,724	57,220,155
DUTCH EAST INDIES.*		
Ficus, plantation product, exported from—	Kilos.	Guilders.
Java and Madura	124,345	435,208
Sumatra—		
East coast	440,170	1,540,595
Borneo—		
Western	66,102	231,357
South and East	99,143	347,001
Ficus, not plantation product, exported from—		
Sumatra—		
East coast	13,539	40,617
West coast	514	1,542
Borneo—		
West	3,129	9,387
South and East	3,774	11,322
Hevea, exported from—		
Java and Madura	2,345,047	8,207,665
Sumatra—		
East coast	3,036,430	10,627,505
Borneo—		
South and East	5,459	19,107
Ceara, exported from—		
Java and Madura	10,671	32,013
Hevea, dried, in sheets, exported from—		
Java and Madura	84,481	5,069
Castilloa, exported from—		
Java and Madura	43,766	100,662
Other, exported from—		
Java and Madura	45,894	100,697
Sumatra—		
East coast	9,943	21,875
Borneo—		
West	26,964	59,321
South and East	170,951	376,092
STRAITS SETTLEMENTS.		
Borneo rubber, exported in—	Piculs.	S. S. dollars.
1913	8,195	752,966
1914	3,055	220,911
Gutta-percha, exported in—		
1913	70,303	4,755,134
1914	43,317	2,008,082
Gutta, inferior, exported in—		
1913	155,858	1,451,082
1914	124,306	1,063,300
India rubber, including Rambong, exported in—		
1913	4,973	554,762
1914	3,892	261,798
Para rubber, exported in—		
1913	199,474	28,466,030
1914	332,043	41,205,828

*Year 1913.

American glass manufacturers who have felt the necessity of depending upon foreign clays will be able hereafter to assert their independence of foreign material, as a result of experiments that have been conducted by the United States Bureau of Standards. The Pittsburgh laboratory of that bureau, which is located near one of the chief centers for the industry in the United States, working in co-operation with the clay-pot industries, has learned that glass refractories (pots in which the glass is melted) can be prepared from American clays, with resulting better quality than that of the article manufactured with the addition of German plastic clays. The mixture prepared from American clays proved superior in the glass-corrosion tests, both to the mixtures prepared with German clays alone, and to those prepared from American and German clays combined. The director of the Bureau of Standards states that the value of the results of this single investigation to American industry far surpasses the entire amount the Government has expended in the clay-products work since the time of its organization. The opinion of those in charge of the experiments is that from now on no foreign clays will be needed in this branch of manufacture. The work inaugurated by these experiments is now ready to be tried out on a large scale.

METALLURGY.

ELECTRIC FURNACE MELTING OF FERRO-ALLOYS.*

By R. S. WILE.†

Among the many things that this war has brought about is the high price of metals. This is due to several causes: large consumption abroad, inability to receive shipments, and embargoes by foreign countries. Among the metals whose prices have soared are the ferro-alloys of manganese, silicon, chromium, etc., the chief source of supply of which is broad.

With these alloys reaching high figures, and with bad business conditions in this country, it becomes necessary to use less alloy or to raise the price of steel. As neither of these is advisable under existing conditions, more economical methods of using them must be sought, and for that purpose we are exploiting our electric furnaces.

One way of doing this is to melt the ferro-alloy before adding it to the ladle, thereby saving a large part of the metal usually lost, and also improving the steel by avoiding segregation because of thorough distribution. This also means easier working of the steel.

The work we have been doing in ferro-alloys is not confined to open hearth practice alone, but in melting the alloys for other practices as well.

Mr. Skinner, of the Westinghouse Co., was at Niagara Falls last October when I was demonstrating a furnace for the smelting of tin dross, and he suggested that I get in touch with him upon my return, which I did. We sent a small furnace out to their plant for demonstrating and it was used for several purposes, among them being the melting of nickel-iron for casting grid resistances. It is necessary to keep a high graphite content in the iron to maintain its toughness, and to have the specific resistance of one heat similar to another in order to do away with the tedious testing and sorting of the heats, so that they will correspond. These requirements are rendered more difficult by the high temperature necessary to pour the very thin castings demanded. Great care must be exercised to prevent the change from iron to steel at this temperature, for while the iron is very tough the steel is very brittle, hence it can readily be seen that there are some requirements which would prevent the use of some kinds of furnaces for melting this material. The tests in the small furnace warranted their installing a larger one of 500 lb. capacity per heat. A grid cast from this furnace is shown.

The largest use for our furnace is, however, for open hearth practice.

A condition which occurs in most steel plants is a variable supply of power due to the electrical equipment being used intermittently. A furnace of the slag resistance type can be used to good advantage for melting ferro-alloys during these periods of idleness, as it can be retarded or advanced at will without serious damage other than delaying the melting of the alloy, but as the composition of the alloy does not change during melting it does not affect the material in the least to keep it in the furnace longer, the only inconvenience being in the case of several furnaces being ready to tap in quick succession, in which event it is necessary to draw upon the power supply. The advantage of melting the alloys is apparent in almost every instance, but more particularly where large additions must be added to fifty-ton ladles, causing a decrease in the temperature of the steel, often rendering it necessary to tap the ladle before the additions are thoroughly distributed. Not only does this make working difficult but it makes it necessary to stock the part not conforming to specifications. The handling of this steel and the inconvenience caused would greatly offset the cost of the electric furnace and its operation, without figuring in the saving of metal, which must be taken into account at any time, but more particularly now that the cost has advanced.

This country has never given much attention to the manufacture of special steels, most of these having come from abroad, but now that the supply has stopped more attention is being given it here, but it finds us largely unprepared. Very few mills are so equipped that they could add 3,000 lbs. of ferrochromium to a 50-ton heat of steel. Even though they could handle it, there would be no certainty of the composition when it was tapped, and it is for these cases mentioned that our furnaces have found application.

I will give a brief description of the furnace before going into results, in order that its operation may be clearly understood. The furnace is of the three-phase type, one bottom and two top electrodes. The spacing of the electrodes is such that they compose, as nearly as possible, an equilateral triangle. To start, the two top electrodes are lowered to the floor of the furnace, some granular graphite or plumbago is sprinkled in and when this glows the slag-making materials are added. These vary with the material, but window glass is used for most purposes, as it is neutral to most of the metals to be melted. As this melts the electrodes are raised until the proper height is reached, and the alloy is then charged into the furnace and is melted beneath the slag from the heat of the bath and not from the direct heat, as in the case of the arc furnace. No auxiliary mechanism is used, the current coming direct from the transformer to the furnace, the heat being regulated by the depth of the electrodes in the slag. When the metal is melted it is either poured into an auxiliary ladle and thence into the steel ladle, or the entire electric furnace is picked up by the auxiliary hoist of the crane and the furnace poured as if it were a ladle. The slag stays in the furnace to be ready for the next heat. It retains its molten condition for a considerable length of time, which enables the power to be quickly picked up again. If the furnace is used as a ladle it is set down by the auxiliary before the big ladle is poured, and is either picked up by another crane and put into place or kept where it is until the ladle is poured and then replaced. This latter course, however, dissipates a good deal of valuable time and is not conducive to the highest efficiency of the furnace.

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It may be questioned by many as to the advantages derived from introducing the alloy in a molten condition, other than those of distribution, etc. I mean the saving of metal effected. The percentage of saving varies with the amount of manganese added to the steel. As is well known, a great part of the manganese added to both open-hearth and particularly Bessemer steel is lost in freeing the steel of oxides and the amount of manganese oxidized is less with a high carbon than with a low carbon steel—it decreases with the amount added. Thus, if 1.00 per cent manganese be added to the bath, 0.60 will be found in the steel (loss 0.40); if 0.60 per cent be added the steel will retain 0.40 (loss 0.20). The loss in one case is 40 per cent and the other 30, and there is no assurance that all parts of the steel will show 0.60 per cent or 0.40, as the case may be. The function of the manganese then is two-fold, one to reduce the oxides, but mainly to strengthen the steel, but tests and practice have shown that by adding the manganese while molten the losses shown above do not occur so heavily, and that a larger percentage of the manganese is retained in the steel. The saving is often as much as 35 per cent of the manganese used.

The following extracts from an article by Felix Schröder, of Livet, France, giving the results of melting over 1,000 tons of ferro-manganese are interesting and give some idea of the cost in an arc furnace. The costs of doing this in the resistance furnace are somewhat less as later figures will show.

The results obtained with one furnace of the Keller system at the Burbacherhütte in Saarbrücken are described. It was adopted there after previous tests at the works of Keller-Leleux Company in Livet had shown the possibility of melting 80 per cent ferro-manganese in the electric furnace without any losses of manganese. The furnace was designed for the manufacture of steel and was run alternately on steel and ferro-manganese during the last nine months. The use of molten ferro-manganese was begun at once on a large scale. More than 1,000 tons of ferro-manganese have been remelted in the electric furnace, to be used as molten addition to all basic converter metal, in the ladle, for several months.

The continuous operation of the converter plant during the six week days required an uninterrupted running of the electric furnace in order to have hot ferro-manganese ready whenever needed. On Sunday the metal usually remained in the furnace and was maintained fluid by the electric current, the consumption of electric current for this purpose being "very low." When no electric power was available the furnace was emptied and restarted on Sunday night. During the week the furnace was never emptied. Small repairs were done on Sunday, the hot metal meanwhile being poured into a ladle.

The longest period during which the furnace was used for melting ferro-manganese was three months. During this time the roof of acid brick, which had already been used before during a period of steel refining, was neither repaired nor renewed. The dolomite lining was not renewed, and only a few small repairs were made from time to time. After these three months of ferro-manganese melting the furnace was started to run on steel again, and the lining was still in fair condition. The roof and lining of the furnace when used for melting ferro-manganese, therefore, last at least three months, and the author claims that a lining of magnesite would stand from six to nine months in continuous operation. The inclined lower lining between door and hearth and also the lining of the hearth itself were not changed for nine months, requiring only a few repairs.

From the results obtained at the Burbacherhütte, the following conclusions may be drawn:

1. The remelting of ferro-manganese in the furnace occurs without any losses of manganese by volatilization.

For example, 10 average samples of solid ferro-manganese had the following analysis: 80.29 per cent Mn.

Thirty-seven successive samples of molten ferro-manganese taken from the electric furnace had the following analysis: 80.22 per cent Mn.

The remelting, therefore, causes practically no loss of manganese. There is no smoke nuisance at the furnace.

2. The net saving due to the use of molten ferro-manganese amounts to 35 per cent of the amount of solid ferro-manganese which would be necessary for the production of steel of the same quality and under the same conditions of operation. Another saving results from the fact that all the small pieces and "fines" of ferro-manganese, which are usually lost in ordinary practice, can be used up.

In this comparison it is assumed that the same amount of manganese shall be in the finished steel as in usual practice. As a matter of fact, however, it is possible, if the addition of ferro-manganese is made in molten form, to reduce slightly the manganese content in the finished steel without affecting the rolling quality.

3. Costs of melting based upon a price of 0.5 cent per kw.-hour were approximately \$5 per ton of ferro-manganese, including electric power consumption, electrode consumption, wages, linings, and repairs. These are not the costs of special experiments, but a monthly average, and therefore include costs of heating and starting the furnace, delays, interruptions due to electrode changes, Sunday work, etc., or, briefly, all the expenses of using the process in a commercial basic-converter plant.

Assuming that the melting-cost per ton of ferro-manganese is \$5, the price of one ton of ferro-manganese \$40 only (abroad), and that 5 kg. of ferro-manganese are to be used per ton of steel, we obtain the results given in Table I.

TABLE I.

Yearly production of steel, tons.	Ferro manganese remelted, tons.	Total Melting Cost, dollars.	Saving of Ferro-mang. (if 1 kg. of Ferromang. is saved per ton of steel), tons.	Price of Ferro-manganese saved, dollars	Saving of Ferro-mang. (if 2 kg. of Ferromang. is saved per ton of steel), tons.	Price of Ferro-manganese saved, dollars.
100,000	500	2,500	100	4,000	200	8,000
200,000	1,000	5,000	200	8,000	400	16,000
300,000	1,500	7,500	300	12,000	600	24,000
400,000	2,000	10,000	400	16,000	800	32,000
500,000	2,500	12,500	500	20,000	1,000	40,000
600,000	3,000	15,000	600	24,000	1,200	48,000
800,000	4,000	20,000	800	32,000	1,600	64,000

It may be said that, on account of the smaller ferro-manganese consumption, the weight of steel produced is also smaller. The slag is also less. The useful phosphorus in the slag increases and there is no reduction of phosphorus back into the metal. All these facts have a very small influence on the final results.

The above consumption of 5 kg. ferro-manganese per ton of steel is an assumed figure; it will in reality vary according to the quality of steel produced at different plants, therefore the calculation should be considered only as an example. It shows, however, that in no case do melting costs exceed the saving in ferro manganese, even if only 1 kg. of ferro-manganese per ton of steel should be saved. But the situation is improved considerably if 2 kg. or more of ferro-manganese can be saved.

Besides this, the use of ferro manganese offers many other advantages which should not be overlooked. The desired quality of the steel is far more easily obtained than is possible with the use of solid ferro-manganese. All of the molten alloy is completely absorbed by the hot metal. With some experience in estimating the manganese contained in a sample of converter metal taken after the blow, it becomes easy to determine accurately the amount of ferro-manganese to be added. This is of great value for high-carbon steels.

Using solid ferro-manganese on cold heats in the converter, one always runs the risk of it not being absorbed in the bath, but using molten additions, the distribution of molten ferro-manganese in the ladle is uniform, the deoxidation quick and more effective, and rephosphorization impossible.

Not only is the quality of the steel improved, but the capacity of the converter plant can also be increased, since the time required for the resting of the metal to permit the ferro-manganese to dissolve is saved. The gain per heat is always a few minutes, which amounts to something when running full capacity.

There is no reason why this process should not be successfully employed in open-hearth practice.

We have carried out extensive tests to prove that there is no change in the alloy while melting, and to show the carbon electrode and power consumption, as well as the cost of linings, in our furnace, and we have come to the following conclusions, using 80 per cent ferro-manganese to be added. This is of great value sumption is nearly 800 K. W. H. per ton; the carbon electrode consumption is never over 12 lbs. per ton and rarely that; the lining cost is between 10 and 25 cents per ton, depending upon the rapidity of melting. This means that the cost, with power at 0.5 cent per kilowatt hour and carbon electrodes at 4 cents per lb. will be between \$4.50 and \$4.75 per ton, exclusive of labor, which is incidental to the plant anyhow. This will add to the cost of the average steel between 3 and 10 cents per ton—a very small amount, which is easily compensated by the reduced handling. Another point of saving is in closer calculations of the manganese, in this manner, as stated before. If the specification calls for 1 to 1.25 manganese the proper amount can be melted to yield the 1 per cent in the steel, thereby saving the 0.25 per cent.

Most of these remarks have been confined to ferro-manganese, but the saving in ferro-chromium is easily greater, as this alloy is now charged into the steel while in the open hearth, where the loss is greatly increased. Without an electric furnace it is necessary to do this owing to the high melting point of the alloy and the impossibility of its becoming melted by the time of pouring the ladle. It is truly wonderful to contemplate the saving possible by pre-melting this alloy.

I have taken up a great deal of time in the matter of the alloys, and I will pass quickly over the smelting of Bolivian tin ores and concentrates. As you doubtless know, this has never been done on a commercial scale in this country. In the countries where it was smelted it was done in reverberatories, and the slags which were basic in character were re-treated in blast furnaces. These slags carried from 15 to 20 per cent of tin before re-treating, and from 2 to 3 per cent after re-treating. The tin ran about 95 to 96 per cent pure. We were required to smelt a lot of these concentrates, which we did, using an acid slag with a loss of 1.89 per cent tin in the slag or 0.5 per cent of the tin content, recovering tin which ran 98.75 per cent pure, without any refining and with an expenditure of less than 450 kilowatt hours per ton of concentrates. A smelter is now under way for handling these concentrates in this city. At present the ores are over-concentrated, and it is necessary for us to add silica and other fluxes to them, these fluxes having been originally in the ore. The analysis of the concentrates treated was as follows:

Tin	66.96
Silica	5.24
Iron	0.92
Sulphur	1.14

ELECTROCHEMICAL SYNTHESIS OF PHENYLHYDROXYLAMINE.*

By F. M. FREDERIKSEN.

Snowden[1] has pointed out that the chemical and electrochemical methods of reducing nitrobenzene are by no means similar though, in general, they should be. At the suggestion of Professor Bancroft, I have made a few experiments to fill one gap in the case of phenylhydroxylamine. Bamberger[2] prepared phenylhydroxylamine chemically by heating nitrobenzene for a few minutes with zinc dust and water. The yield varies very much—from 0 to 57 per cent of the theoretical. Bamberger calls attention to the fact that different samples of zinc dust give very different yields even though the content of metallic zinc be the same and even though all other conditions are kept the same. Thus, one sample of zinc dust gave aniline and no phenylhydroxylamine. Bamberger considers that these enormous differences may be due in part to the fact that one sample of zinc dust gives chiefly molecular and therefore inactive hydrogen. Another way of wording the same thing is to say that different impurities in the zinc affect the over-voltage differently. The best yield was obtained by adding ten grams of nitrobenzene to half a liter of boiling water, throwing in 75 g. zinc dust (about 67 per cent metallic zinc) all at once, boiling for three-quarters of an hour, cooling rapidly and saturating with sodium chloride. The phenylhydroxlamine was shaken out with ether, the ether distilled off, and the crystallized oil washed with ligroin. The yield was 57 per cent of the theoretical. Other products are azoxybenzene, azobenzene, and aniline.

The question of yield is also discussed by Wohl,[3] who has discovered the reaction independently of Bamberger. At first, nitrobenzene was heated for twenty minutes with ten times its volume of water and an excess of zinc dust. With 50 per cent of zinc dust a yield of about 12 per cent phenylhydroxlamine was obtained. When three times the theoretical amount of zinc was taken, the yield increased to about 20 per cent. It is not feasible to heat for a long period because azoxybenzene, azobenzene, and aniline are then formed.

It was found that salts like calcium chloride, magnesium chloride, and zinc chloride accelerate the reaction between zinc dust and nitrobenzene. According to Wohl, this is because they form insoluble salts with zinc hydroxide. To obtain the best yield 250 c.c. per cent aqueous alcohol was heated in a flask with reverse cooler. To the flask was added 60 g. nitrobenzene and then 6 g. anhydrous calcium chloride, after which 75 g. commercial zinc dust was added in the course of fifteen minutes. The contents of the flask were heated for about five minutes after the last of the zinc dust was added, and were then cooled and filtered. The alcohol was distilled rapidly from the filtrate until an oil layer appeared which solidified on cooling. About 70-75 per cent of the theoretical yield of phenylhydroxylamine was obtained in this way.[4]

Wislicenus and Kaufmann[5] found that a 38 per cent yield of phenylhydroxylamine could be obtained by reducing nitrobenzene in 90 per cent alcohol with amalgamated aluminum. In a later paper Wislicenus[6] points out that better results are obtained with an ether solution. Nitrobenzene is dissolved in at least ten times its volume of ether, freshly prepared amalgamated aluminum is added and then water, a little at a time. The flask is equipped with a reverse cooler and is placed in ice to prevent the ether from foaming too much. When one starts with 20-30 g. nitrobenzene the yield of phenylhydroxlamine is said to be quantitative.

Bamberger and Knecht[7] obtained an 85 per cent yield of phenylhydroxylamine (3.8 g.) by dissolving 5 g. nitrobenzene in 50 c.c. 90 per cent alcohol and adding, first a solution of 12 g. aluminum sulphate in 100 g. water, and then 250 g. of a 5 per cent zinc amalgam. The mixture was shaken vigorously for two hours, the temperature being kept below 5°.

I repeated Wohl's work, heating 250 c.c. of 60 per cent alcohol with 60 g. nitrobenzene and 6 g. $CaCl_2$ (ammonium chloride is just as good) on a water-bath in a flask equipped with a return condenser. After bringing the solution just to boiling, 95 g. zinc dust was added through an interval of fifteen minutes, the temperature of the water bath being regulated so that the liquid in the flask boiled gently while the reaction was taking place. Five minutes after all the zinc dust had been added the reaction mixture was cooled, first with running water and then with ice. The mixture was filtered by suction and the zinc oxide washed with about 50 c.c. alcohol. The alcohol was boiled off until the temperature of the distilling vapor reached 86°, this being about the point at which the solution clouds owing to the separation of an oil. When the solution is cooled in a freezing mixture, the phenylhydroxylamine separates in crystals contaminated with some azobenzene. The crystalline mass, colored a bright orange by the azobenzene, was filtered by suction and then washed with ligroin. The washing must be done with care because phenylhydroxylamine is somewhat soluble in ligroin. The azobenzene is removed practically completely, leaving the phenylhydroxylamine almost pure and white. The yields varied between 30 and 40 per cent, which is in accord with the results of Bamberger.[8]

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*Paper presented at the 28th General Meeting of the American Electrochemical Society, in San Francisco, Sept. 16-18, 1915.

[1] Jour. Phys. Chem., 15, 797 (1911).

[2] Ber. deutsch. chem. Ges., 27, 1348, 1548 (1894).

[3] Ber. deutsch. chem. Ges., 72, 1432 (1894).

[4] Bamberger states that he has never been able to average more than 35 per cent yield in this way and that the maximum observed was 50 per cent. Ber. deutsch. chem. Ges., 29, 864 (1896).

[5] Ber. deutsch. chem. Ges., 28, 1326, 1983 (1895).

[6] Ibid., 29, 494 (1896).

[7] Ibid., 29, 863 (1896).

An attempt was now made to duplicate the reaction electrolytically by using zinc electrodes in an ammonium chloride solution. Of course a zinc anode is not essential theoretically; but it obviates the use of a diaphragm and cuts down the voltage considerably. Since it would be difficult to use electrodes having a surface equal to, say, 100 g. zinc dust, the reaction must take longer. In order to prevent the decomposition of the phenylhydroxylamine, which would probably occur if the solution were kept heated a long time, it was deemed advisable to run at a low temperature.

The solution was placed in a 300 c.c. beaker and stirred during electrolysis by means of a spiral stirring rod run by a motor. After the reduction had gone on as long as desired, the solution was filtered through a Büchner by suction and the alcohol then distilled off as in the chemical reduction. On account of the smaller amounts of substance taken, the solution was not cooled and filtered, but was saturated with sodium chloride and extracted with ether. The ethereal extract contained the phenylhydroxylamine and azobenzene with only a trace of salt or of ammonium chloride. The ether was driven off and the residue was crystallized from a small amount of benzene to which ligroin was added after solution and filtration. Phenylhydroxylamine is very soluble in hot benzene and only slightly soluble in cold benzene. Addition to the benzene of an approximately equal volume of ligroin cuts down the solubility a great deal. The azobenzene remains in solution.

Theoretically it requires 107.2 ampere hours (4x26.8) to reduce one molecular weight of nitrobenzene (123 g.) to phenylhydroxylamine. Since nitrobenzene has a specific gravity of 1.2, 10 c.c. nitrobenzene is approximately 12 grams and calls for 10.46 ampere hours, which should give 10.73 grams phenylhydroxylamine.

The following results were obtained:

Run 1: 250 c.c. 60 per cent alcohol, 12.5 g. ammonium chloride, 10 c.c. nitrobenzene. Zinc electrodes. Cell packed in ice. Average temperature 12°. One ampere for 9.5 hours. No stirring for the first hour. Yield, 28 per cent.

Run 2: 250 c.c. 60 per cent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell cooled in running water. Average temperature 14°. 0.75 ampere for 6.7 hours. Yield, 21 per cent.

Run 3: 250 c.c. 60 per cent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell cooled in freezing mixture. Average temperature —5°. 0.75 ampere for 6.7 hours. Yield, 20 per cent.

Run 4: 250 c.c. 60 per cent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell cooled with running water. Average temperature 19°. 2 amperes for 2.67 hours. Yield, 29 per cent.

Run 5: 250 c.c. 60 per cent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell not cooled. Average temperature, 36° C. 4.8 amperes for 1.11 hours. Yield, 22 per cent.

These yields are all lower than those for the chemical reduction; but part of this difference is undoubtedly due to the fact that the losses are greater when 6 g. nitrobenzene is used instead of 60 g. in the same amount of solution. Also, we do not know what the reduction efficiency of the zinc dust is, though that could be determined; but we know that it is necessary to use more than the theoretical amount of zinc. The time at my disposal did not permit me to make runs to see what effect an excess of ampere hours would have.

It is possible to tell something about the results during the run. If much hydrogen is evolved at the cathode or if much zinc is precipitated there, the efficiency is necessarily low. A deep red color to the solution shows a considerable formation of azobenzene, an orange color a much less formation, and a light yellow color hardly any formation of azobenzene.

GENERAL CONCLUSIONS.

1. It is possible to reduce nitrobenzene to phenylhydroxylamine electrochemically without the use of a diaphragm, by using a zinc anode.

2. The chemical process of reducing nitrobenzene to phenylhydroxylamine with zinc dust can be duplicated electrochemically.

3. The yield from the electrochemical process is less at present than the yield from the chemical process. Part of this difference is due to the fact that the percentage losses are larger the smaller the amount of nitrobenzene taken.

4. The efficiency of reduction and the conversion to azobenzene both decrease with falling temperature. One has to strike a mean therefore between slight conversion to azobenzene, but low reduction efficiency and high reduction efficiency with high conversion to azobenzene. The best results so far have been obtained at about room temperature.

Phosphate of lime deposits have been discovered in the Banff National Park, Canadian Rockies.

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[8] Ber. deutsch. chem. Ges., 29, 864 (1896).

THE PEPTONIZATION OF CHROMIC OXIDE.*

By WILDER D. BANCROFT.

Fischer and Herz[1] point out that the addition of an excess of caustic soda or potash to a green solution of chromic chloride gives rise to a clear green solution, because the precipitated hydrous chromic oxide apparently dissolves in the excess of alkali. On long standing, the solution becomes cloudy through precipitation of hydrous chromic oxide. This precipitation takes place more slowly the greater the excess of alkali. It takes place more rapidly, the higher the temperature. These facts, together with the difficulty of redissolving the chromic oxide in alkali caused Fischer and Herz to suspect that the apparent dissolving of chromic oxide in caustic alkali was really a peptonization. On that assumption no alkaline chromite is formed.

Fischer and Herz made dialysis experiments and conductivity experiments to confirm this hypothesis. "An alkaline solution of chromic hydroxide was prepared by adding an excess of caustic soda to a chromic chloride solution. This was dialyzed against pure water using animal bladder as a membrane. All the experiments showed that the water outside soon became alkaline but remained colorless for several days. A heavy precipitate of chromic hydroxide formed on the membrane. The alkaline solution of chromic hydroxide thus behaves like a typical colloid as opposed to a similar solution of aluminum hydroxide in caustic soda which contains a true compound, the aluminum diffusing perceptibly through the membrane. * * *

"As a further confirmation of the view that chromic hydroxide is peptonized by caustic solutions, measurements of the electrical conductance were made, the underlying idea being that the electrical conductance of a solution of chromic hydroxide in caustic soda must depend on the caustic soda if the chromic hydroxide is in colloidal suspension. The precipitation of the chromic hydroxide can only affect the conductance slightly. If a compound is formed, the precipitation of the chromic hydroxide involves a decomposition of the dissolved and conducting compound and must therefore cause a change in the conductance. Since the precipitation of chromic hydroxide from a caustic soda solution can easily be brought about by boiling, the experiments were carried out in the following way:

"To a solution of green chromic chloride sufficient caustic soda was added to dissolve the precipitate first formed. The electrical conductance of this solution was then determined. The solution was heated and the precipitated chromic hydroxide filtered off. The conductance of the filtrate was determined and it was found that heating and filtering had not changed the conductance. * * * From these experiments it follows with great probability that a colloidal solution is formed when chromic hydroxide dissolves in caustic soda, whereas alumina forms a compound under similar conditions. Zinc hydroxide seems to be an intermediate case, being present in alkaline solutions partly as zincate and partly in colloidal form.

"If these experiments are repeated, starting with chromic sulphate solution instead of with chromic chloride solution, there seems to be complications which are probably due to the formation of chrome sulphuric acids and which have not been studied in detail."

While Fischer and Herz are undoubtedly right in their conclusion, some details of their experiments are not above criticism. In the first place it is not correct theoretically to say that the precipitation of the hydrous chromic oxide will have no effect on the conductivity of the solution. In so far as the hydrous chromic oxide is peptonized by hydroxyl ions, the adsorption of these ions must produce some change in the conductivity. When the hydrous chromic oxide precipitates, it carries down with it an indefinite amount of water and of alkali, which must also have an effect. It is possible, of course, that the removal of the alkali is counterbalanced practically by the removal of the water; but that can only be a coincidence and cannot be true generally. What is more likely is that the change of conductivity fell within the limit of experimental error, since there was present a large excess of caustic soda. One would have felt more confidence in the unpublished data if Fischer and Herz had not obtained results which agreed admirably with their faulty theoretical conclusions. It seems desirable therefore to confirm their results by other experiments and this has been done for me by Mr. Nagel.[2]

Fischer and Herz state that an alkaline solution of hydrous chromic oxide becomes turbid on standing, owing to the precipitation of the oxide and that this precipitation takes place more slowly the greater the excess of caustic alkali; but they do not say how great the precipitation is, apparently because they were more interested in the fact that practically complete precipitation can be obtained in a short time by heating the solution. Mr. Nagel treated freshly precipitated hydrous chromic oxide with an excess of caustic potash to prevent jelling, and set the solutions away in glass-stoppered bottles. At the end of three weeks a large amount of green precipitate had formed, but the liquid was still green. At the end of two months the solution was only faintly yellowish green, the bulk of the chromium oxide having precipitated. There is therefore a slow agglomeration and precipitation of the peptonized oxide, the rate of agglomeration being cut down by the excess of the peptonizing agent, the hydroxyl ions.

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*Paper presented at the 28th General Meeting of the American Electrochemical Society, in San Francisco, Sept. 16-18, 1915.

[1] Zeit. anorg. Chem., 31, 352 (1902).

[2] Jour. Phys. Chem., 19, 621 (1915).

Filtration experiments have also been made, using a Bechhold ultra-filtration apparatus[3] and collodion filters. The hydrous chromic oxide is filtered out completely from an alkaline solution, the filtrate coming through colorless. While there may be some adsorption by the filter, this is of no importance because the filtration was carried on until hydrous chromic oxide was left in mass on top of the collodion filter and could be scraped off from it. Chromic chloride solution, on the other hand, runs through green, the dissolved salt not being removed.

This raised the question as to what one has in a so-called basic chromic solution. When hydrous chromic oxide is heated with a chromic chloride solution, some of the chromic oxide seems to go into solution. With an ultra-filter the chromic chloride solution passes through, while the hydrous chromic oxide is filtered out. It is therefore clear that a so-called basic chromic chloride solution contains hydrous chromic oxide peptonized, but not dissolved, by chromic chloride. There is no evidence that any appreciable amount of basic salt is formed in solution, though no quantitative measurements have been made in regard to this.

Mr. Nagel also tried to shake out peptonized chromic oxide with benzene or kerosene, but this proved impossible in alkaline solutions. When precipitated oxide is shaken with water and benzene, it goes into the dineric interface;[4] but addition of caustic alkali causes it to precipitate, presumably because the alkali is itself adsorbed by the organic liquid.[5]

Fischer and Herz[6] state that an alkali chloride has very little effect in precipitating hydrous chromic oxide peptonized by caustic soda, but that it has a marked effect in precipitating hydrous chromic oxide peptonized by barium hydroxide. This is undoubtedly due to the fact that the bivalent barium ions are adsorbed more strongly than the univalent sodium ions and consequently make the peptonized oxide more nearly neutral and less stable. I should expect to find that barium hydroxide has a lesser peptonizing action than caustic soda. This experiment was not tried by Fischer and Herz; but they showed that caustic potash has a greater peptonizing action than caustic soda, which proves that the concentration of hydroxyl as ion is not the sole factor in peptonization. In line with this is the fact that hydrous chromic oxide peptonizes hydrous ferric oxide and is carried down by it.[7]

GENERAL CONCLUSIONS.

1. Using a collodion ultra-filter it is possible to filter out the hydrous chromic oxide peptonized by caustic alkali.

2. On long standing, nearly all of the peptonized chromic oxide precipitates from a caustic alkali solution.

3. Chromic chloride solutions peptonize hydrous chromic oxide. No appreciable amount of basic chloride appears to be formed.

4. It is not possible to shake out hydrous chromic oxide from an alkaline solution either with benzene or kerosene, even though benzene will remove hydrous chromic oxide from water.

5. Since hydroxyl ions are the active peptonizing agents with hydrous chromic oxide, a strongly adsorbed cation will decrease the stability of the colloidal solution.

5. The order of decreasing stability is potassium, sodium, barium, iron.

Cornell University.

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[3] Bechhold: Zeit. Phys. Chem., 60, 257 (1907); 64, 328 (1908).
[4] Bancroft: Jour. Phys. Chem., 19, 275 (1915).
[5] Wilson: Jour. Chem. Soc., 1, 174 (1848); Twomey: Jour. Phys. Chem., 19, 360 (1915).
[6] Zeit. anorg. Chem., 31, 355 (1902).
[7] Nagel: Jour. Phys. Chem., 19, 331 (1915).

IRON DEPOSITS OF BRAZIL.*

Although geographically nearly as large as the United States and in many places highly mineralized, Brazil is almost unexploited as a mining proposition. The mining laws of the country have recently been remodeled in a manner that provides a decided step toward modernization and practical applicability, but this legislation will not overcome the lack of transportation facilities from the interior and the high cost of freights and of labor, which have hitherto been obstacles sufficient to keep the truly great mineral resources of the Republic almost untouched. [An analysis of the new mining law referred to may be examined at the Bureau of Foreign and Domestic Commerce or its branch offices; ask for file No. 60286.]

Of Brazil's iron ores, the hematites are in Minas Geraes, Matto Grosso, Goyaz, and Bahia; the magnetites (some titaniferous) in Sao Paulo, Parana, Santa Catharina, and Rio Grande do Sul. The most important deposits by far are those of the State of Minas Geraes.

EXTENT OF DEPOSITS—RAILWAYS.

Through the central part of Minas Geraes extends the Serra de Espinhaco in a northerly-southerly direction. In this range of mountains are found nearly all of the mineral deposits of the state. The great iron area seems really to be within a well-defined rectangle, 56 miles long by 37 miles wide, with Burnier on the south side, Sabara on the north side, and Santa Barbara and Marianna on the east. In addition to the ores within this rectangle, scattered deposits extend northerly toward Diamentina, so that the high-grade iron-bearing formations probably occupy an area of some 2,200 square miles. If the lower-grade deposits are also considered, the area will be doubled in extent.

Three railroads either tap or are projected to tap this district. The most important is the government-owned line (the Central Railway), which enters the iron area near its southwestern limit at Burnier and extends northward to Sabara. It also has branches extending from Burnier to Marianna and from Sabara to Santa Barbara. From Rio de Janeiro, the nearest seaport, to Burnier is about 370 miles, and to this point the road is broad gauge (5.25 ft.), while from Burnier to the other points the road is reduced in gauge to 3.28 ft. Another railroad, the English-owned Leopoldina, does not enter this main rectangle, but is built to tap the deposits at Itabirra de Matto Dentro, north of the rectangle. Its seaport is also Rio de Janeiro, and the distance from Rio to Itabirra is about 390 miles. Still another railroad, French owned, is partially constructed to operate between the seaport Victoria and Itabirra de Matto Dentro, a distance also of about 390 miles.

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*From Daily Commeree Reports.

CLASSIFICATION OF ORES—PROBABLE TONNAGE.

The ores may be classified as follows:

1. Bedded ores.—(a) Very thick, bedded, massive hematite, including the dense, hard blue and the fine and coarse specular varieties and martite. Beds are up to 300 feet in width and a mile in length. (b) Thin bedded, laminated hematite, fine grained or crystalline, hard and soft. Beds not so wide as (a), but have great length.

2. Fragmental ores.—(a) Canga, a conglomerate of hematite pebbles cemented together with limonite. (b) Extensive beds of hematite "float" (rubble). (c) Sand ore; "float" mixed with sands in river bottoms and elsewhere.

3. Secondary ores, carbonates, etc.

The important ores commercially are the bedded hematites, both thick and thin, the Canga conglomerates, and the rubble ores.

In order to give some idea of the extent of the deposits, the Servico Geologico do Brazil selected nine of the largest and entirely exposed deposits and computed the cubic contents of each separately. These are of the bedded (highest grade) type, and are not assumed to have an extension below the surface of the surrounding country. On this basis they gave an estimated tonnage of 988,000,000. Dr. Orville Derby, the director of the Geological Service of Brazil, thinks this figure can conservatively be doubled, which tonnage about equals the total reserve of the Lake Superior ores today.

In addition to the above estimated tonnage, which includes the highest grade ore only, there are known to exist millions of tons of the lower grade Canga and rubble ores. One deposit of rubble is estimated to contain 20,000,000 tons, while the Canga ores, running higher than 50 per cent iron, would perhaps total 1,710,000,000 tons.

The total output in the first 10 months of 1915 of six Dutch rubber companies was 818,213 lbs., as compared with 530,944 lbs. in the calendar year 1914. The returns for each month, in most of the reports, show an increase for 1915 over 1914.

AMERICANS BUY NORTH CAROLINA ALUMINUM PLANT.

The transfer of a large American aluminum plant from foreign to American ownership is announced in press reports from Charlotte, N. C. French interests were active throughout the greater part of 1914 in pushing extensive operations at the Narrows of Yadkin River, near Whitney and Badin, Stanley County, N. C., but as a result of the European war the development of the property stopped and was expected to be at a standstill for an indefinite period. In buying the plant the Aluminum Co. of America, with headquarters at Pittsburgh, Pa., announces that the development work will be resumed, and that the plans of the original designers will be carried out with only slight modifications.

In its last report on the aluminum industry the United States Geological Survey stated that the work that the Southern Aluminum Co. had in progress at Badin and Whitney consisted of a hydroelectric installation of great size for the generation of electric power, and electrolytic plant of large capacity for the production of metallic aluminum, works for the purification of alumina, an electrode factory, and the homes and other buildings necessary for the well-being of the large number of employes engaged in an important undertaking of this kind.

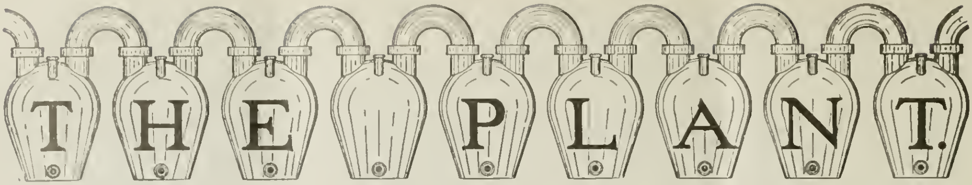
It was early in 1913 that a contract was let for a concrete dam and power house, for tunnels, and for the grading of the electrolytic plant sites. The plans provide for a dam 220 ft. high, 1,300 ft. long, 160 ft. thick at the base, and 20 ft. at the crest. Swinging as the arc of a circle of 1,600 ft. radius, its construction involves the use of from 550,000 to 600,000 cu. yds. of concrete. This great dam will store water to generate from 20,000 to 70,000 kilowatts, according to water stage, and will form a pond of 5,000 acres. With the reservoir full, the river will be held in check for 5 miles along its course, and the old granite Whitney dam will be entirely submerged.

Before the work on this plant was stopped by the war, there were 2,500 men employed on the construction. After production commences, it has been estimated the number required will be between 1,200 and 1,500.

The Aluminum Co. of America has plants at Maryville, Tenn., and Messena, N. Y., and has also acquired interests at Edgewater, N. J.

The growing importance of this metal is shown by the figures relating to exports for the last fiscal year. During the 12 months ended June 30, 1915, the exports of aluminum and its manufactures were valued at $3,245,799, compared with $1,101,920 in the preceding year, and with $1,046,915 in the year ending with June, 1913.

India ranks sixth among the world's cotton yarn manufacturers, having 6,800,000 spindles.



A SUMMARY OF THE EXPERIENCE GAINED IN THE TREATMENT OF THE WASTES FROM THE SCOURING OF WOOL.[*]

By HARRY R. CROHURST[†] and ARTHUR D. WESTON.[††]

The production of woolen goods from the raw wool involves the processes of sorting the wool fibre as it arrives at the mill and the cleaning or scouring of the fibre to remove the impurities always contained in it, so that it can be spun or woven into the finished product. These processes vary considerably because of the great variety of the goods produced and the differences in the raw materials used. In the production of the goods the following preparatory steps are usually carried out: Sorting, dusting, picking, carbonizing, scouring.

After the removal of the impurities and the production of a clean fiber it is then spun into yarn or woven into cloth. This process involves the following steps: Oiling, picking, combing, spinning, weaving.

The finishing process consists of a second scouring to remove foreign substances added to assist in the spinning and weaving, and the fulling or dyeing to produce the finished product.

Wastes are produced from the processes of scouring and finishing. The waste from scouring is a dirty brown liquor high in suspended matter, containing a large amount of wool fat and considerable potassium salts in solution. The wastes from finishing consist of the scouring solutions used for the cleaning of the goods previous to fulling and dyeing, the scouring solutions and rinse waters after fulling, and the spent dyes and rinse waters from the coloring operations. It is the purpose of this paper to deal principally with the treatment of the liquors produced in the process of scouring the raw wool. In a later paper the authors will take up the treatment of the wastes from the finishing processes.

In order that the engineer may have a better understanding of the character of the wastes produced, it may not be out of place to give here a brief outline of the structure of the wool fiber, the various classes of wool, the impurities encountered at the mills and the processes used in finishing the raw fiber.

The term wool is sometimes broadly applied to the covering of many animals, but is usually applied to the covering of sheep which is the most important of the fibers used in the textile industries. The wool fiber has its root in a gland in the middle layer of the skin and is produced by a secretion of lymph-like liquid. This gland also secrets an oil which softens and lubricates the fiber. Other glands secrete the wool fat which forms a protective coating on the fiber and prevents matting. The length and diameter of the wool varies not only in the different species of sheep but also in the individual animal. The length varies from 1 to 8 ins. and the diameter from .0018 to .0040 in. Wool fiber is divided into two grades—"Tops" and "Noils." Tops contain the long staple fibers which are combed and spun into worsted yarns and then woven into dress goods, etc., but are not fulled to any extent in the finishing. The noils contain the short staple fibers which are carded and spun into woolen yarn to be used in goods which are fulled in the finishing.

Wool used in this country comes from nearly all parts of the world. The quality depends upon the breed of the animal, climatic conditions, the nature of the pasturage and the physical condition of the sheep.

COMPOSITION OF WOOL.

The composition of wool fiber proper is very similar to that of hair, horn, feathers and other epidermal tissues. Omitting the dirt, dried sweat and grease and considering the pure fiber, it is made up of combinations of carbon, hydrogen, oxygen, sulphur and nitrogen. While it has no definite chemical formula, an average of its composition may be approximated as follows:

	Per Cent.
Carbon	50
Hydrogen	7
Oxygen	26-22
Nitrogen	15-17
Sulphur	2- 4

IMPURITIES OF WOOL.

The wool fiber as it is received at the mill contains a large percentage of impurities. To show the amount of pure fiber obtained from the raw Merino wool, which is considered to be of rather high quality, "Chevreul" gives the following analysis:

	Per Cent.
Earthy matter deposited by washing in water	26.06
Suint and yolk soluble in cold distilled water	32.74
Neutral fats soluble in ether	8.57
Earthy matter adhering to fat	1.40
Wool fiber	31.23
Total	100.00

The above per cent of pure fiber is based on wool dried at 100° C. Air dried wool conntaining 14 per cent moisture would yield about 27 to 28 per cent pure fiber. The impurities consist of yolk, suint and earthy matter. The yolk and suint are usually classed together. The suint is that portion of the impurities which can be removed with water and consists of the dried perspiration deposited on the fiber. This is made up chiefly of potassium salts, oleic acid and other fatty acids. Potassium in the form of carbonates, sulphates and chlorides is also present. It will be seen that the removal of these impurities which are soluble in water forms a solution valuable for the recovery of potash salts.

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Stabler & Pratt in Water Supply Paper No. 235 give the following average of the soluble salts recovered from the water used in the steeping of wool previous to scouring:

SALINE COMPOSITION OF POTASH RECOVERED FROM WOOL STEEP LIQUOR.

Per Cent of Crude Potash.

	Per Cent.
Potassium carbonate, K_2CO_3	74.6
Potassium sulphate, K_2SO_4	3.2
Potassium chloride, KCe	9.5
Potassium silicate, K_2SiO_3	8.2
Sodium carbonate, Na_2CO_3	3.7

The yolk or wool fat is composed of ethereal salts of cholesterol and isocholesterol and salts of fatty acids (oleic, stearic and palmitic). This wool fat is insoluble in water but can be dissolved by volatile solvents, as carbon bisulphide, naphtha, benzine, etc., or as an emulsion by the aid of alkaline detergents. Here again the solution from the removal of the grease offers a chance for the recovery of a valuable product.

The Massachusetts State Department of Health in their experiments upon the effect of wool scouring wastes upon the Merrimack River give some figures upon the amount of recoverable material contained in the waste. Table I is made up from these data.

The earthy matter consists of sand, dirt, etc., adhering to the wool mechanically. The amount depends upon the soil from which the wool is produced and varies from 3 or 4 per cent to 30 or 35 per cent of the weight of the wool. There are also present in the fiber, dung, burrs, grass, straw, etc. The following estimate by a New England scourer shows the average makeup of raw wool received at the mill: Soil 20%, dung 5%, moisture 12%, grease 23%, clean fiber 40%, total 100%.

Following is the makeup of German wool: Mineral matter 6.3%, suint or yolk 44.3%, moisture 11.4%, clean fiber 38.0%, total 100.0%.

The raw wool received at the mill will contain anywhere from 30 to 80 per cent of impurities which must be removed before the fiber can be spun and woven into the finished product. The removal of these impurities is carried out in the process of wool scouring.

SORTING.

The wool as it arrives at the mill is spread upon a sorting table and graded according to the requirements of the material to be made. The sorting tables are provided with a screen top and a heating system (used generally in the cold weather when the grease solidifies making the fiber stiff and difficult to sort). Solid material easily removable passes through the screens and the larger foreign matter is cut from the wool. The wool is sorted according to the length and fineness of the fiber which is dependent on the part of the sheep from which it comes.

DUSTING, PICKING AND CARBONIZING.

The sorted wools containing dust and fine material are generally run through a dusting machine. By the aid of a fan this machine removes fine dirt, straw, etc., the larger particles of foreign matter dropping out through the bottom. Where the wool contains large burrs in considerable numbers it may be run through a burr picker or where the burrs are small the wool may be carbonized by soaking it in dilute sulphuric acid. This disintegrates the vegetable matter of the burr and on drying and passing through rolls is ground to dust and removed in the dusting machine. After carbonizing the wool must receive a neutralizing bath and it is then ready to be scoured.

As already stated, the wool at this point contains

TABLE I.—AMOUNT OF RECOVERABLE MATERIAL CONTAINED IN WOOL SCOURING WASTES.

Mill.	Bowl.	Quantity of waste, gals. per day.	Per cent of total waste from bowls 1 and 2.	Lbs. per day, fat.	Per cent of total fats found in bowls 1 and 2.	Lbs. per day, potash.	Per cent of total potash found in bowls 1 and 2.	Bowls 1 and 2. Lbs. in each 1,000 gals. Fats.	Potash.
Lower Pacific	1 and 2	24,845	..	5,471	..	1,633	..	...	..
	All 4	72,015	35	5,797	94	1,751	93	220	66
Washington	1 and 2	44,675	..	5,705	..	3,498	..	...	..
	All 4	130,591	34	5,941*	96	3,570*	98	130	78
Kunhardt	1 and 2	1,566	..	189	..	45	..	...	..
	All 4	22,569	7	251†	75	50†	90	120	29
Lewis	1 and 2	51,888	..	7,158	..	3,485	..	...	..
	All 4	58,909	88	7,406	97	3,555	98	138	67
Ayer	1 and 2	32,108	..	4,494	..	2,502	..	...	..
	All 4	35,877	89	4,528	99	2,510	99	140	78
Wood	1 and 2	55,651	..	5,863	..	3,179	..	...	..
	All 4	119,364	47	6,430	91	3,313	96	105	57

*Does not include 56,000 gals. per day discharged from 4th bowl.
†Does not include 10,500 gals. per day discharged from 4th bowl.

all the wool grease and potassium salts which are recoverable. Where an attempt is made to recover any of these products it can be done at this stage. Steeping the wool in warm water will remove the soluble potassium salts which can be recovered by evaporation and incineration of the steep water. If volatile solvents are used in scouring this will remove the wool grease which can be recovered. Where no preliminary steps are made for the recovery of products the wool is run directly to the scouring machines and the resulting waste water, containing all the wood grease and potash, may be treated as described later for the recovery of the products.

SCOURING.

The ridding of the wool of grease and dirt is carried out in wool scouring machines and the process is called scouring. The methods now in use are the primitive single bowl process and the modern method consisting of scouring in a machine with several bowls. The old method consisted in lowering the wool in a cage into the scouring liquor and stirring or "poling" it to insure the liquor reaching all parts of the fiber. After remaining in the liquor until the grease and dirt were removed the fiber was withdrawn, drained and then put into a rinse box and washed in clean water. The modern method, which is carried out in the mechanical wool washer, is more rapid and economical. The machine is divided into four—sometimes three—compartments called bowls which contain the scouring liquor and the rinse water which are kept heated to about 100° F. The modern type of four-bowl machine is sometimes known as the "Parallel Rake Wool Washing Machine." The machines are made in various sizes. The bowls are either 16, 27, 32 or 37 ft. long and 2, 3 or 4 ft. wide. A mill scouring about 15,000 lbs. of grease wool a day, which has a shrinkage of 60 per cent, would use a four-bowl machine 4 ft. in width, the length of bowls being, No. 1, 37 ft.; No. 2, 27 ft., and Nos. 3 and 4, 21 ft. The first two bowls would be used for scouring and the last two for rinsing.

Scouring Agents.—Alkali and soap are the agents commonly used and the amounts of each vary in different mills and with the quality of the wool being scoured. As an example of the solutions used the following formula for the soap solution and amounts used is given by a wool scourer. The wool assumed to be in the machine has a shrinkage of about 60 per cent. The amount scoured is 12,000 lbs. per day in a four-bowl machine.

ALKALI SOLUTION (SOAP).

Dissolve 25 lbs. of caustic potash in 100 gals. of water.
Add water to make up to 300 gals.
Add 100 lbs. of red oil, which will produce a jelly-like mass.

SOAP SUDS.

1 lb. of soap to every 2 gals. of water.

If each bowl has a capacity of 800 gals. the following amounts of solutions should be added:

Bowl 1. 80 lbs. soda ash, 36 gals. suds and add water to make up to 800 gals

Bowl 2. 10 lbs. of soda ash, 18 gals. suds and add water to make up to 800 gals.

Bowl 3. No soda ash, 12 gals. of suds and add water to make up to 800 gals.

Bowl 4. Running water.

In the operation of such a machine the suds are renewed every hour and the soda ash in the middle of the morning, at noon and the middle of the afternoon. When the liquid in the first bowl becomes muddy it is discharged and the liquor from bowls 3 and 2 is pumped forward to bowls 2 and 1, after which the strength is made up and new liquor is added to the third bowl.

The outline for solutions used in a three-bowl machine is as follows:

ALKALI SOLUTION (SOAP).

400 lbs. caustic potash dissolved in 100 gals. of water.
Add water to make up to 400 gals.
Add 100 gals. of red oil, forming a jelly.

SOAP SUDS (SCOURING LIQUOR).

Boil 125 lbs. of soap, 200 lbs. of pearl ash and 250 gals. of water until all are dissolved.

Using three 16-ft. bowls for very greasy wool, use 12 pails of scouring liquor in the first bowl, 10 pails in the second bowl and clear water in the third bowl.

Stabler & Pratt have estimated that for each 1,000 gals. of water 40 to 50 lbs. of soft soap and 5 to 10 lbs. of potash were generally used to scour from 1,000 to 2,000 lbs. of wool to produce 600 to 900 lbs. of wool fiber. The raw wool is fed continuously into one end of the scouring machine and by a series of moving rakes is carried forward through the first compartment until it reaches a squeeze roll where the liquid it has taken up in passing through this compartment is squeezed out of it. It then passes into the second compartment and through the machine in a similar manner. The water from the first compartment receives the greatest amount of dirt and when too concentrated to be of further use is discharged. The water from the second and third compartment is then pumped forward into the first and second compartments, respectively, more reagents being added to make up the strength of solutions, and fresh solution added to the third compartment. The last compartment may in

TABLE II.—SHRINKAGE OF VARIOUS WOOLS DURING SCOURING.

Grade of wool.	Shrinkage. Per Cent
Washed fleeces:	
Ohio and Pennsylvania	50-52
Texas	58-65
Georgia	34-42
Lake	40
Grease California	55-65
Eastern Oregon	61-62
Valley Oregon	50
Graded territory:	
Arizona	55-66
Colorado	62-64
Dakota	58
Idaho	62-70
Montana	60-63
Nevada	65-70
Utah	62-66
Wyoming	65-72
New Mexico	65-66
Australia:	
Choice Sydney	56-57
Choice Geelong	51-52
Average Sydney	50
Average Queensland	52
Choice New Zealand	25-30
South America:	
Montevideo	48-50
Buenos Aires	48-50

some cases be supplied with running water which washes the scoured wool after passing through the solutions in the first three compartments. The waste from the machine is, therefore, a very concentrated, dirty brown liquor containing large amounts of suspended matter, grease and the reagents used in scouring. The wastes from these bowls may be separated, that from the fourth passing directly into some stream and the concentrated liquor from the first stored for the recovery of valuable products as described later; or as is the common practice both are discharged into a nearby stream and if the flow is small the effects are noticeable considerable distances below the point of discharge. Analyses of the liquor in each of the bowls of the scouring machines are given later in a table.

Shrinkage.—During the process of scouring the wool shrinks on an average of about 60 per cent. Table II shows some of the grades of wool handled in this country and the shrinkage during scouring.

OILING AND PICKING.

After scouring and washing the fiber is dried in a centrifuge, or by passing hot air through it, or by both methods. Scouring leaves the wool harsh and brittle and before being finished the fiber is softened by oiling. At this point any mixing of the different grades of wool or other fibers which is necessary for the various kinds of materials produced is carried out. The mixed fibers are run through a "mixing picker" to obtain the necessary blend and may be oiled at the same time. The oil is added to replace the wool grease which has been removed during scouring and lubricates the fibers, prevents waste in combing and spinning and protects the fiber in handling. Olive oil, lard oil, oleine, red oil and certain mineral oils are used in this process, which can be done by hand or in machines. The oil is applied as an emulsion.

COMBING, SPINNING AND WEAVING.

Carding is the first of several processes which collectively are known as combing. It consists of separating the fibers, arranging them in a continuous sliver, all parts of which are equal in weight, thickness and quality and contain fibers of every length. After the combing process the wool which has taken up some dirt in the operations may be given another washing and subsequent oiling before being spun. This is called "back-washing" and is usually carried on in a two-bowl machine. There is a small amount of dirt, and pure olive oil soap is used in washing, the dirt being removed by squeeze rolls. The water used in back-washing is small in quantity compared with that used in the wool washing. Probably the quantity is less than one-tenth of the quantity used in the wool scouring operation. Because of the small quantity and the small amount of dirt and grease contained in it, this water used in back-washing has very little effect on the character of the heavier liquor if the two are combined. After dyeing the wool is oiled again and is ready for spinning. The remaining operations consist of preparing the warp, in which there are several steps, and the weaving into the finished goods.

FINISHING.

After the goods come from the looms the remaining processes through which the different grades and classes of goods pass are called finishing. These operations consist of fulling, washing, dyeing, etc. The wastes from these processes will be discussed in a later article by the authors.

QUANTITY OF WOOL SCOURING LIQUOR.

In Table III, made up from the data of the Massachusetts State Department of Health in their examination of the Merrimack River, will be found the quantity of wool scouring liquor based on 100 lbs. of wool scoured. While these figures may give some indication of the average quantity of waste per pound of wool scoured, it is always well to bear in mind that there are many grades of raw wool, all varying in the per cent of impurities that they contain and that the amount and character of the waste depends on the grade of raw fiber in the machine.

In the four-bowl machines the average quantity of water used per 100 lbs. of wool scoured amounts to approximately 147 gals., or roughly 1½ gals per pound of wool scoured. The figures for the three-bowl machines show that about 86 gals. of water are used per 100 lbs. of wool scoured, or slightly less than a gallon per pound of wool scoured. The method of operating these machines, as already described, varies considerably. In all mills the concentrated waste is discharged from the first bowl, the water from the sec-

TABLE III.—QUANTITY OF WOOL SCOURING LIQUOR PER 100 LBS. OF WOOL SCOURED.

Mill.	Bowl.	Waste, gals. per day.	Quantity of wool scoured per day in lbs.	Waste per 100 lbs. wool scoured.
Pacific	1	17,080	......	44
	2	7,765	38,692	20
	3 & 4	47,170	......	122
Total		72,015	......	186
Washington	1	31,427	......	37
	2	13,348	84,463	16
	3 & 4	85,916	....	102
Total		130,691	.	155
Lewis	1	34,923	......	51
	2	16,965	68,359	25
	3	7,021	......	10
Total		58,909	.....	86
Ayer	1	21,646	.....	56
	2	10,462	38,460	27
	3 & 4	3,769	......	10
Total		35,877	......	93
Wood	1	30,427	......	40
	2	25,224	77,099	33
	3 & 4	63,713	.....	82
Total		119,364	......	155

ond and third bowls being advanced to the first and second bowls so that the discharge occurs at intervals from the first bowl and contains all the impurities in a concentrated solution. Usually the last bowl contains only wash water which is constantly passing through the machine and running to waste. Sometimes the last two bowls are operated in this manner in which case only about 46 per cent of the total water used, or about 68 gals. per 100 lbs. of wool scoured, would consist of the heavy offensive wool liquor.

The analyses of the wastes from the various bowls of the machine show that bowls 3 and 4 contain only a small percentage of the impurities found in the first two bowls. The analyses show, however, that the liquor from the last two bowls is usually stronger than domestic sewage. About 95 per cent of the recoverable material is contained in the liquor of the first two bowls, or, as the liquor of bowl 2 is pumped into bowl 1 before being discharged, 95 per cent of the recoverable material is in the discharge from the first bowl.

QUALITY OF WOOL SCOURING WASTES.

In Tables IV-VIII is given the composition of various wool scouring liquors from several different sources.

Tables IV and V are made up from many samples collected by the Massachusetts State Department of Health in their study of the pollution of the Merrimack River at Lawrence. These tables show the character of the waste from each bowl of the scouring machines, the average of all the bowls and show the character of the wastes from several mills in the State.

(To be concluded.)

TABLE IV.—AVERAGE ANALYSES OF WOOL SCOURING WASTES FROM THE MILLS AT LAWRENCE, MASS.

Parts Per Million.

		Residue on evaporation				Ammonia.			Kjeldahl nitrogen.				
	No. of samples in average.	Total residue.		Loss on ignition.			Albuminoid.						
Source.		Total	Suspended	Total.	Suspended.	Free.	Total.	Suspended.	Total.	In solution.	Oxygen consumed.	Hardness.	Fats.
				Lower Pacific Mill.									
First bowl	16	92,490	51,510	69,680	45,150	151	409	161	1,153	607	5,311	9,640	46,300
Second bowl	9	23,840	13,700	17,800	11,070	39	134	63	385	192	1,728	2,590	10,010
Third bowl	7	5,700	2,900	4,130	2,280	9	44	26	108	49	574	790	2,960
Fourth bowl	10	940	470	680	400	3	16	11	27	811	107	170	290
Average of third and fourth.	2	2,620	1,280	1,870	1,000	12	28	17	65	25	215	410	750
Average of four bowls	6	39,030	23,040	26,720	16,730	75	210	118	493	257	1,662	3,980	15,690
				Washington Mills.									
First bowl	13	107,670	65,670	55,530	33,100	413	435	162	1,408	680	6,581	10,690	27,730
Second bowl	9	17,020	9,880	12,290	7,920	69	108	51	309	161	1,390	2,010	6,960
Third bowl	9	3,810	1,810	2,530	1,520	13	22	11	79	32	342	520	1,960
Fourth bowl	5	1,650	860	1,170	720	5	36	21	45	16	184	230	620
Average of four bowls	7	35,510	17,980	23,250	13,900	224	226	92	536	299	2,780	4,800	12,060
				Geo. E. Kunhardt Mill.									
First bowl	12	78,420	43,840	48,250	30,840	161	480	211	1,190	663	5,515	10,130	24,330
Second bowl	9	17,460	9,720	10,990	7,030	51	115	57	296	146	1,040	5,860	6,120
Third bowl	5	1,190	380	810	340	80	11	5	25	16	162	630	400
Fourth bowl	5	110	......	60	......	1	0.5	0.2	2	1	10	80	30
Average of third and fourth.	1	1,050	940	500	460	3	10	9	19	2	49	50	60
Average of four bowls	4	30,710	15,120	15,610	7,920	103	200	103	631	295	2,760	4,980	12,030
				E. Frank Lewis Mill.									
First bowl	13	79,440	41,180	42,120	23,760	185	489	212	1,062	624	4,603	14,730	20,100
Second bowl	10	41,340	17,900	20,280	11,070	94	244	96	463	262	2,010	12,780	10,160
Third bowl	11	16,190	6,590	7,490	4,140	21	73	36	191	93	940	6,440	3,520
Average of three bowls	7	51,110	26,030	26,380	15,550	130	232	96	630	302	2,818	12,140	11,400
				Ayer Mill.									
First bowl	9	74,050	29,210	48,830	23,610	371	467	125	1,326	888	7,010	11,140	15,880
Second bowl	9	13,820	7,940	10,270	6,410	33	109	43	296	186	1,170	1,700	5,000
Third bowl	6	4,870	2,350	3,630	1,990	9	49	21	131	64	370	660	1,440
Fourth bowl	6	2,360	1,050	1,740	950	4	26	14	61	28	234	400	880
Average of third and fourth.	3	3,210	1,700	2,380	1,420	7	29	15	71	37	397	370	850
Average of four bowls	6	28,730	12,570	19,680	10,360	145	191	67	541	389	2,080	4,420	7,340
				Wood Worsted Mill.									
First bowl	14	73,710	42,670	39,780	23,120	399	470	183	1,015	491	4,940	8,860	19,010
Second bowl	8	20,730	13,980	13,540	9,060	34	104	49	379	157	1,500	2,000	6,220
Third bowl	5	3,510	1,800	2,550	1,570	5	24	13	69	36	347	640	1,560
Fourth bowl	9	1,010	480	720	420	3	10	7	27	11	96	200	390
Average of third and fourth.	3	3,120	1,920	1,990	1,360	9	29	18	66	28	353	330	1,070
Average of four bowls	5	23,530	11,720	14,850	8,260	115	114	15	413	239	1,481	3,370	7,720

TABLE V.—ANALYSES OF WOOL SCOURING LIQUORS FROM MILLS IN MASSACHUSETTS.

Parts Per Million.

Total residue.		Loss on ignition.			Kjeldahl nitrogen.			
Total.	Dissolved.	Total.	Dissolved.	Free ammonia.	Total.	In solution.	Oxygen consumed.	Fats.
95,542	40,382	73,310	24,460	109	1,326	655	5,747	51,350
69,070	36,570	40,190	16,800	32	1,273	672	3,136	20,090
217,903	47,593	78,613	24,013	157	2,299	869	9,383	41,500
39,147	21,780	24,520	11,834	296	647	348	2,950	16,560
95,000	36,900	13,700	14,020	560	....	...	....	.....
43,020	35,950	11,580	4,910	68	....	...	....	.....
109,980	81,860	......	......	2,400	....	...	....	.....
55,950	18,780	33,490	17,020	66	....	...	6,650	15,956
19,384	5,699	8,968	5,918	20	....	...	1,550*	.....
73,860	43,040	45,020	21,220	720	....	...	6,300	.....

*Filtered.

ELECTROLYTIC BLEACH PLANTS FOR PAPER MILLS.*

By F. G. WHEELER.†

For the manufacture of white paper pulp, the use of chloride of lime has become almost universal. In earlier times pulp was bleached by means of chlorine gas, which was produced by the action of sulphuric acid upon a mixture of salt and black oxide of manganese. The difficulties of this process have been overcome in later years by the use of "bleaching powder." In dry form this substance is unpleasant to handle, and there are many losses connected with its use. As a consequence several pulp mills have been led to make their own "bleach" in liquid form at the mill.

The methods commonly used are modifications of the principle of electrolyzing a common salt solution and passing the liberated chlorine gas into milk of lime, making in this way a bleaching solution, similar to the one made by dissolving dry bleach in water. There is formed simultaneously a solution of caustic soda, which can be utilized or sold as local conditions may decide.

The general idea of a bleach plant is to use this process as an auxiliary to the pulp mill, supplying bleach for use on the pulp. While this view is a natural one for the manufacturer of pulp, it is an unnatural one for the "bleach" maker, and it is with this thought in mind that I would draw attention to possible advantages which might be gained from this last idea.

The electrolytic process is a more or less complicated one, having frequently as many distinct operations as the manufacture of the pulp itself. The salt is purchased by the carload, and this must be unloaded and made into a solution. Power must be brought from some central station or made separately for the bleach. The brine and the electricity are brought together, caustic soda and chlorine gas being formed by the contact. The lime must be slaked and made into a milk. The chlorine gas is absorbed in this milk, after which it is settled, and the clear supernatant liquid is delivered to the bleachery. The sludge is worked over and over until the lime is used up. The caustic soda solution is concentrated, and delivered as a strong solution or is brought to the solid form to be sold as such. Each part of the process has its own problems. It would seem therefore that the manufacture of bleached pulp should be considered as a whole unit, the pulp mill adapting its operation to that of the bleach plant and bleachery in order to make the best conditions for the manufacture of the final product.

All who have handled chlorine gas are familiar with its corrosive nature. There are but few substances that can withstand its action, so that the design of the cell is one which has provoked much thought in the past, and there are many variations in the detailed design of this part of the process. There are, however, two general principles which obtain in all the work. The first is low renewal cost. Those parts of the cell which become useless through corrosion must be so made that their renewal is a minor part of the process. The second principle is low operation cost which means that labor and power must be kept at the minimum, as well as the loss of material. While these two principles apply to all processes in a general way, they are particularly noteworthy in a bleach plant. The variations which can be made in such a process are almost infinite, and the success or failure of an installation depends upon the proper adaptation of these to the particular application.

To elaborate this idea more fully, the raw materials may be considered as so much salt, lime, power, labor and coal. If the salt is the most expensive item, the process should be designed and arranged to keep the salt losses at a minimum, sacrificing other materials to save it. If, on the other hand, power is expensive, the cells should be so designed that they have a high efficiency, using a low voltage, and every effort should be made to keep the power cost down, letting other losses take place if it will save power. It happens, however, that many mills have excess waterpower, and labor is difficult to get. The sacrifices can then be made on the power end, to save on the number of men required to care for the plant, and machines can be used to replace the hand labor. Under certain conditions it is of advantage to run the cells continuously and, where this is possible, large storage capacity will pay for the savings to be made. In this particular case, the arrangement of the pulp mill work will assist materially. It might also make it worth while to have the mill go into the manufacture of other chlorine compounds so that the bleach plant can be operated as a paying proposition apart from the pulp manufacture.

The formation of the caustic soda simultaneously with the chlorine sometimes introduces problems which make the installation of a process difficult. Many times the statement is made that the caustic soda can readily be disposed of, either as a liquor or in solid form, but this does not always work out well in practice. Strong caustic soda solutions have been used by many of the firms who make soap, and the conclusion seems to be that the finishing, or solidifying of the caustic eliminates impurities which are in the strong liquors so that the use of the solid caustic in the manufacture of soap seems preferable. The process of solidifying caustic is a trade in itself, and it is not so simple a process as it might appear. The trade generally wish a pure white caustic, and the shading is a problem at times. To keep the half finished caustic from frothing, and to know just when to apply heat or not are points worth examining before considering an installation of this kind.

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*From Paper.

†Chemical Engineer, Kimberly-Clark Co., Neenah, Wis.

The design of the plant should be made so that standard apparatus can be used as far as possible. Any chemical process of this nature requires a large amount of special material. In some instances the inclination has been to make all the other parts of the process dependent upon the way these special parts work out. It would seem, however, that since these are special anyway, the rest of the plant should be made standard. Take the cell, for instance: this must be special, each part being made to meet the object of the designer. The power apparatus is a standard machine made by many different manufacturers. The cell, therefore, should be the one to be adapted to the plan, and not the electrical machinery. This latter should be of a standard voltage and winding, while the cell can be made to take a current at that voltage, so that the capacity of the plant is what is desired. The motors and lighting system can then all be operated from the same busses. As already pointed out, the cell should also be designed to have a high or low efficiency, using power or labor in proportion to the respective costs, so that the overall can be made a minimum. In this way a cell plant can frequently be adapted to a mill where arbitrary units do not show an advantage.

In conclusion, it would appear that a bleach plant might be made an advantage to a pulp mill by the observance of two general principles. These are: first, the adjustment of each of the various factors within the bleach plant which keep the final costs low, or the real commercial efficiency high; and second, the adaptability of the pulp mill to those conditions which favor this commercial efficiency in the plant.

The Anaconda Copper Co. is now reported to be producing electrolytic zinc at the rate of 10 tons per day. It is reported that a large plant for this purpose is to be erected near hydroelectric power. The production of spelter by electricity has not been profitable heretofore, but several important factors favor this enterprise by the Anaconda company. The ore is also relatively high in silver, a large part of which is recoverable, and electric power there is cheap. The pure product also commands now a very high price, rivaling tin. As made by Brunner, Mond & Co., at Winnington, Eng., heretofore the only makers of electrolytic zinc, it is guaranteed 99.95 per cent zinc.

Platinum deposits recently discovered in Spain and said to be among the richest in the world, have been turned over to the government by the discoverer. Chromium and nickel are also present. Concessions to exploit these mines are to be granted to foreigners as well as Spaniards.

THORIUM[*]

By THURSTON OWENS.

Three hundred million gas mantles consumed annually throughout the world are dependent upon the supply of thorium. Some eighty million are used yearly in the United States, double the quantity consumed ten years ago. These and other valuable facts are brought out in a recent publication of the Bureau of Mines, prepared by Mr. Karl L. Kithil.[*†]

The property of emitting light radiations in the visible part of the spectrum, under the application of heat, has been known and applied for over a century,[†] but it was Dr. Auer von Welsbach who discovered (1886) that thorium had the unusual quality of holding together, without other materials being used as a support,[‡] hence the mantle mesh.

It was not until 1891 that Dr. Auer perfected his formula of 99% thorium and 1% cerium, which produced the highest light efficiency and also the nearest approach to white light in color. For 25 years the mantles used by the gas industry have been produced with this formula as a base; another of the many features of continuity and stability which characterizes the industry.

Thorium is one of the constituents of monazite sand, the others having great chemical interest, but little commercial value (Whitaker). There are numerous occurrences of Monazite Sand throughout the world, but it has only been mined successfully in North and South America (Kithil). This last statement is open to question as the deposits at Travancore, India, have been the subject of considerable British wrath in the past few months.

"Germany, by underhand as well as straightforward methods, was steadily proceeding towards the fulfilment of her ambition to control the thorium supply of the world when war broke out." The article from which this is quoted goes on to explain how the Auer Company obtained a controlling interest in the leases at Travancore, which was nullified by an edict of the Secretary of State for India reducing the voting power of the "enemy shares," and instructing the company to sell all purchasers upon an equal basis. The British India sand which has reached this country is reported to be far superior to the Brazilian product. The mining of monazite sand in America has been practically abandoned since 1906, and none of the large users see any commercial possibilities in this field.

In order to obtain thorium two definite steps are necessary. The first consists of separating monazite from the other materials mined, which is done in the neighborhood of the mine. The monazite sand is then shipped to the laboratories of the mantle manufacturers where the thorium is manufactured.

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[*] From American Gas Light Journal.

[*†] Monazite, Thorium and Mesothorium, technical paper 110, Bureau of Mines, Dept. of the Interior, Washington.

[†] The Rare Earths, Their Occurrence, Chemistry and Technology. S. I. Levy.

[‡] Incandescent Gas Mantles. M. C. Whitaker, Johns Hopkins Lectures on Illuminating Engineering.

"The manufacture of nitrate of thorium from monazite sand is a very difficult and complicated chemical process. It requires from 4 to 6 months to recover the small percentage of thorium and render it sufficiently pure to be used in the manufacture of lighting fluid" (Whitaker).

The treatment of monazite for the extraction of thorium, described by Soddy§ is as follows: After the sand has been ground the cold mass is dissolved in water and left to settle. The solution is then fractionally precipitated with magnesia, the thorium being concentrated mainly in the first fractions precipitated. The commonest and most useful reagent for precipitating the rare earths from a solution containing common earths, such as alumina, iron, etc., is oxalic acid. Now thorium oxalate is of all the rare-earth oxalates the least soluble in acids, so that by working in fairly strong nitric acid solution, thorium oxalate may often be precipitated and separated, at least partially, from the other rare earths and from calcium. The same is true of the rare-earth phosphates, that of thorium being one of the most insoluble in dilute acids. On the same principle, thorium is often precipitated by weak bases, such as the substituted ammonias, for example, dimethylamine, while zirconium, etc., remain dissolved. The potassium salt of hydrazoic acid KN_3, precipitates thorium hydroxide only from mixtures of thorium and cerium on boiling. The same separation may be effected by means of sodium thiosulphate on boiling, thorium alone being separated, as hydroxide. This ready hydrolysis of weak thorium is characteristic of the element. The oxalates of thorium and zirconium alone of the rare earths are soluble in ammonium oxalate, and on strongly acidifying the solution, the former alone is reprecipitated. The solution of the oxalate of thorium and its conversion into soluble salts may be effected by means of concentrated ammonium or sodium carbonate and precipitation of the concentrated solution as thorium hydroxide with strong ammonium or sodium hydrate. Thorium is distinguished from the yttrium group of the rare earths by its power of forming a double sulphate with potassium sulphate, insoluble in excess of the latter reagent, and so may be separated from a mixture of the sulphates by saturating the solution with potassium sulphate. Alike in the old, now obsolete, as in the present, technical methods of purifying thorium, the peculiar solubility relations of thorium sulphate in water have been largely applied. The older method consisted in volatilizing the excess of sulphuric acid from the material being treated, and in dissolving the anhydrous sulphates in ice-cold water—a tedious operation—and in heating the solution till the hydrated thorium sulphate was precipitated. The latter was then dehydrated at 300° to 400° and the process repeated. In present practice the sulphuric acid is always kept in great excess in the initial treatment of the mineral, but the sulphate method may be employed at the final stage of manufacture as follows:

The thorium hydroxide is dissolved in hydrochloric acid, so that the solution contains not more than 30% ThO_2, and sulphuric acid is added to the extent of 0.5% more than the equivalent quantity, the temperature being kept low, and in any case below 40° as a maximum. Under these conditions the hydrate $Th(SO_4)_2 8H_2O$ is precipitated, departure from the conditions causing the separation of the tetrahydrate, which is in every way less easily manipulated. The precipitated sulphate is converted into hydroxide, and the process repeated as often as necessary to remove all impurities.

Thorium forms a curious compound with acetyl acetone, $Th(C_5H_7O_2)_4$, which is soluble in chloroform and alcohol, and can be distilled in a vacuum, and so can advantageously be employed for the purification and separation of the element.

It may be mentioned that in the fusion of refractory minerals, as with sodium carbonate, the thorium, if present, is converted into the highly insoluble oxide, ThO_2, and its presence is apt to be overlooked.

Thanks largely to the thorium industry, in which a product unusually pure is essential, there exist therefor a great variety of exceedingly good and sharp methods for the separation and purification of thorium, and it must be understood that ionium, if present, and radio-thorium always remain unseparated from thorium in these processes as far as they have been examined.

In the manufacture of thorium nitrate from monazite a large amount of residues of the cerium group of rare earths is obtained. Monazite containing 60% to 70% of the cerium group or other rare earths besides thorium, and 3,000 tons, which is the annual consumption of monazite, gives about 1,000 tons of cerium and about 1,200 tons of a mixture of the rare earths lanthanum, neodymium and praesodymium oxides. Considerable research work has been done in order to utilize these waste materials, and experiments have been made with almost every one of them. In order to obtain and separate the rare earth elements, thousands of crystallizations and fractionations are necessary, although cerium itself is separated with comparative ease. The untiring work carried on in the research laboratories of the industries as well as by the scientists in both America and in Europe will, no doubt, in time be crowned with successful technical applications of the by-products.

The monazite resources are given by Kithil as follows:

It is difficult to give even a rough estimate of the quantities of monazite obtainable in the various countries. From close calculations, however, it is estimated that the lands in the marinhas along the seacoast of Brazil may yield from 15,000 to 20,000 tons of pure monazite. This does not include coast lands where the deposits have been formed in comparatively short time.

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§The Chemistry of the Radio Elements, Frederick Soddy.

In the interior of Brazil the writer knows of about 18,000,000 of monazite-bearing gravel deposits which should yield monazite containing 4½ per cent of thorium oxide; and it can be estimated that these gravels contain 45,000 to 60,000 tons of monazite. No doubt there will be found many other deposits of greater or less extent in the interior of Brazil, but no single deposit in the interior, so far as known, would warrant the erection of a large plant. In sections where several large deposits are found together, or near each other, a washing and concentrating plant might be profitably established, provided the price for the monazite obtained were higher than at present (May, 1915), and especially if transportation facilities from the interior to the coast become better.

The amount of purified monazite available in the Carolinas may be conservatively estimated at about 15,000 to 20,000 tons (4½ per cent ThO_2).

With better methods of mining and refining, perhaps these deposits could be profitably exploited at the present prices for monazite and thorium nitrate, especially if the mining of monazite were carried on in connection with the manufacture of thorium nitrate and mesothorium.

It is known that attempts have been made to extract the monazite from the native rock, but this operation with even the richest rock known—0.1 to 0.2 per cent of monazite—has proved too expensive.

Duty on Monazite Exported from United States and Brazil.—There is no duty on monazite exported from the United States.

The duties on monazite exported from Brazil vary greatly, and are as follows:

Federal Government.—Duty on monazite from the marinhas—situated along the entire coast and navigable rivers of Brazil—is charged at the rate of 50 per cent ad valorem ,and is fixed at £30, or about $150, per ton. Individual states have fixed duties, as follows:

Rio de Janeiro.—Approximately $21 per metric ton.

Espirito Santo.—80 per cent of selling value, established to be £25 per ton. This duty is varying and is subject to reduction when applied for.

Minas Geraes.—12 per cent ad valorem, fixed at £25 per ton and 25 per cent ad valorem, fixed at £25 per ton, plus £2 specific duty.

Imported Duties.—The duty on monazite imported into the United States has been 6 cents per pound, but was reduced to 4 cents in 1910, and is now 25 per cent ad valorem.

The import duty on mantle ashes is $10 ad valorem.

The import duty on nitrates has been 25 per cent ad valorem.

THE TARIFF.

In view of the increased price of thorium, the Journal has obtained expressions from several of the large users of thorium, regarding changes in the tariff that would forestall any increase in the retail price of the gas mantles.

The opinion seems to be general that as long as the American mantle makers can obtain monazite sand from abroad the prospects of using American deposits are doubtful. On the other hand, a reduction in the tariff on sand and an increased duty on the finished mantle, would do much to stabilize the industry. As an incentive to American manufacturers, the duty is hardly scientific, as it calls for 25 per cent ad valorem on sand, thorium and on mantles.

If we are to be protected from wholesale dumpings, the rates could better be arranged with free ore, 25 per cent duty on thorium and 40 per cent duty on mantles.

THE UTILIZATION OF AROMATIC HYDROCARBONS DERIVED FROM CRACKED PETROLEUM.*

By W. F. RITTMAN.[1]

In the course of the commercial development of the vapor-phase cracking process for the production of benzene and toluene from petroleum, numerous chemical problems have arisen. One of the most important is the utilization of the products obtained, since these necessarily differ from those derived from coal. The idea is widely prevalent that petroleum-derived products are inferior and a principal object of the present work has been to show that this prejudice is due entirely to a lack of knowledge concerning proper methods of utilization.

The immediate cause for the present work has been the necessity of demonstrating that petroleum-derived toluene can be successfully converted into trinitrotoluene in a commercially practicable manner.

DIFFERENCES BETWEEN COAL-DERIVED AND PETROLEUM-DERIVED HYDROCARBON MIXTURES.

A brief consideration of the sources and methods of production of the two types of commercial hydrocarbon mixtures serves to indicate the nature of the present problem.

The coal-derived products are the results of decomposition of the original material at high temperatures, which fact influences to a large degree the composition of these mixtures. The aromatics are associated with varying quantities of such impurities as sulphur, oxygen, and nitrogen bodies, as well as non-aromatic hydrocarbons of various degrees of unsaturation.

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*From The Journal of Industrial and Engineering Chemistry. Published with the permission of the Director of the Bureau of Mines.

[1] Professor of Mechanical Engineering, Columbia University.

Condensable paraffins are not, however, stable at the temperatures which occur during the destructive distillation of coal and these hydrocarbons are, therefore, absent from products derived from this source. It follows, therefore, that aromatic products obtained from coal contain objectionable impurities, from which, however, they may be freed if subjected to treatment by proper physical and chemical processes. On the other hand, the cracking of petroleum yields aromatics which are entirely free from oxygen-containing impurities and which at worst carry only minute quantities of sulphur and nitrogen bodies. The chief and practically the only impurities are olefins and paraffins. These paraffins are necessarily present because maximum yields of toluene and benzene cannot be obtained under conditions which entirely break down these saturated compounds and, furthermore, it is difficult or even impossible to get rid of them completely. Methods of fractional distillation do not effect complete separation and chemical methods are ineffective, since the aromatics are more reactive than the paraffins.

Thus, in attacking the present problem it has been granted that it may be difficult or even impossible to obtain pure aromatics from cracked petroleum. Experiments have, therefore, aimed at devising methods of utilization suitable for the impure products and it now appears that these methods have commercial advantages over those in use for coal-derived products, although the latter substances cannot be treated in the same way as the petroleum products since the sulphur, oxygen, and nitrogen bodies are not chemically inactive, as are the paraffin hydrocarbons.

METHODS OF PREPARATION AND PROPERTIES OF THE NITROTOLUENES.

Trinitrotoluene is obtained from toluene by a process of nitration occurring in three successive stages and involving the intermediate formation of mononitrotoluene and dinitrotoluene.

$$(1)\quad C_7H_8 + HNO_3 \rightleftarrows C_7H_7(NO_2) + H_2O$$

Toluene Mononitrotoluene

$$(2)\quad C_7H_7(NO_2) + HNO_3 \rightleftarrows C_7H_6(NO_2)_2 + H_2O$$

Mononitrotoluene Dinitrotoluene

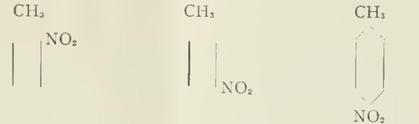
$$(3)\quad C_7H_6(NO_2)_2 + HNO_3 \rightleftarrows C_7H_5(NO_2)_3 + H_2O$$

Dinitrotoluene Trinitrotoluene

The extent to which the nitration may proceed to any one of the above stages is controlled by conditions of treatment and particularly by the factor of acid concentration. This can be regulated by adjustment of the quantity of nitric acid employed and also by varying the amount of sulphuric acid mixed with the nitric to take up and render inactive the water which is one of the reaction products.

PROPERTIES OF THE NITROTOLUENES.

Mononitrotoluene, $C_7H_7O_2$, exists in three isomeric forms, ortho- meta and para:



o—Nitrotoluene *m*—Nitrotoluene *p*—Nitrotoluene

The physical properties of these compounds are indicated below:

Mononitrotoluene—	Melting Point.	Boiling Point.	Specific Gravity.
Ortho	—10.5°	218°	1.168(15°/15°)
Meta	16.0°	231°	1.168(15°/15°)
Para	54.0°	238°	1.231(54°/4°)

Direct nitration of toluene yields a mixture of the three isomers, which, however, contains little of the meta product. This is in accord with the law of substitution in the benzene ring, the methyl group being one which controls the ortho and para positions.

Dinitrotoluene exists in six possible isomeric forms, all solids. These are designated by numbers, the position occupied by the methyl group being No. 1.

Dinitrotoluene	2 : 4	3 : 4	2 : 3	2 : 6	3 : 5	2 : 5
Melting point	70.5°	60.0°	63.0°	61.0°	93.0°	52.5°

The dinitrotoluene produced by the nitration of toluene or of the commercial mixture of *o*- and *p*-nitrotoluenes consists chiefly of the 2:4 and 2:6 products.

Trinitrotoluene is theoretically capable of existing in six isomeric forms. Of these the 2:4:6, the 2:3:4 and 2:4:5 compounds have been prepared. The 2:4:6, or "symmetrical" compound, is the best known and is by far the chief constituent of the commercial product.

Trinitrotoluene	2 : 4 : 6	2 : 3 : 4	2 : 4 : 5
Melting point	80.6°	112.0°	104.0°

Pure nitrotoluene is a white solid of absolutely neutral reaction and of unusual stability. The commercial product is generally pale yellow. Trinitrotoluene is very slightly soluble in water, either hot or cold. It is sparingly soluble in cold alcohol, but readily in hot, this solvent being one commonly used for the process of recrystallization.

Trinitrotoluene is by far the most valuable explosive now used in military service for bursting charges. The substance may be manufactured with comparative safety and is free from danger of deterioration. It is non-acid and does not act upon metals with which it may come in contact. The lowness of its melting point makes easy the filling of shells and containers, which is accomplished by the simple process of pouring the molten explosive. Trinitrotoluene is sufficiently inert so that the possibility of accidental explosion through concussion is practically nil. It is stated that a shell filled with it may be made to penetrate steel plates without setting off the explosive through the shock. Detonation is accomplished after penetration by means of a time fuse.

COMMERCIAL PREPARATION OF TRINITROTOLUENE.

The commercial preparation of trinitrotoluene is accomplished in either of two general ways: (1) The process may be completed in one stage, or (2) it may be accomplished in several successive stages. In any event, it has been found commercially undesirable, in this country at least, to purify the final product by any process of crystallization or washing which involves the use of organic solvents. The purity of trinitrotoluene is generally determined by its melting point and present specifications place this at 75° C., which is about 5° below the melting point of the pure compound. It has been found possible to attain the desired degree of purity by a simple process of water washing, providing conditions of preparation are right.

The single stage process of nitration is of course simple in operation and requires a minimum of plant equipment. It has the decided disadvantage, however, of being uneconomical in acid consumption. The process requires a considerable concentration of acid at the end of the reaction and the resulting spent acid cannot be utilized in the single stage method, although its strength is considerably greater than would be necessary in the earlier stages of the other general process.

Processes involving several stages, with complete or partial purification of intermediate products are, of course, expensive as regards costs of labor and plant equipment. They do, however, permit economic utilization of acid, since the spent acid from the final stage may be employed in an earlier stage of the next cycle, obviating the necessity of discarding any but a thoroughly exhausted waste acid. In addition, as has been shown by the results of the present experiments, the polystage process permits the use of a less expensively purified raw material.

The preparation of trinitrotoluene involves the removal of water-insoluble impurities from the final product or from some one of the other substances, dinitrotoluene, mononitrotoluene, or toluene. Processes involving the use of coal-derived toluene have been dependent upon the purification of the initial substance. In the past, when specifications were more exacting, and especially abroad, crystallization of the final product has been resorted to but this is not practicable under present conditions. The purification of dinitrotoluene involves the same methods as need be applied to trinitrotoluene and that possible medium for purification is likewise eliminated.

SCOPE AND PLAN OF PRESENT WORK.

The present work has been based upon the device of purifying the mono-substitution product. The whole proposition may be stated concisely as follows:

The preparation of satisfactory trinitrotoluene involves a purification from water insoluble impurities of one of the four substances; toluene, mononitrotoluene, dinitrotoluene or trinitrotoluene. Both toluene, and mononitrotoluene are liquids having boiling points sufficiently low that their distillation is a matter involving no inherent difficulty. The purification of dinitrotoluene and trinitrotoluene can be accomplished only through commercially impracticable processes of crystallization or washing which involve the use of organic solvents.

Toluene derived from petroleum cannot be brought to a state of complete purity readily by any methods now known, but by means of simple processes of fractionation it is possible to obtain, from cracked petroleum, toluene with no impurities save paraffin and olefin bodies. The olefins may be removed by extraction with sulphuric acid, and the resulting mixture, when nitrated under proper conditions of acid concentration, yields mononitrotoluene contaminated with the original paraffins, with resinous bodies, formed by the action of the acid, and possibly with a small quantity of dinitrotoluene.

Mononitrotoluene boils between 218° C. and 238° C., the paraffins in the neighborhood of 110° and the resins, etc., at temperatures above 300° C. Hence, a simple distillation, preferably *in vacuo* or with steam, gives an easy and practically complete separation of mononitrotoluene from the low boiling paraffins and the high boiling resins.

Since no water-insoluble impurities are present in the mononitrotoluene it may be converted readily into trinitrotoluene by commercially practicable methods.

EXPERIMENTAL.

Samples of toluene were obtained which had been prepared by simple distillation and redistillation of cracked petroleum from the commercial furnaces employed in the Bureau of Mines vapor-phase cracking process.

Mononitrotoluene—The first section of the work involved the preparation of pure mononitrotoluene and this process was studied in detail. Large quantities were not used, but data were obtained which can be applied with some exactness to commercial work. It was shown conclusively that no difficulties need be encountered in large scale operations. The mononitrotoluene prepared was analyzed carefully for its purity, as indicated by nitrogen content. Yields were also measured, although no emphasis is laid on these since the scale of operation made them necessarily low.

Trinitrotoluene—The analyses of the mono product indicated that it was almost chemically pure but it was thought desirable to actually convert it into the higher substituted compound. Samples of trinitrotoluene were therefore prepared; these, when washed with water, showed melting points of 75° and above. In the course of these preparations valuable indications were obtained as to advantageous methods of procedure for large scale operations, although no final details were worked out.

Nitrobenzene—Finally a simple experiment was performed to verify the obvious conclusion that benzene mixtures would behave in a manner identical with those containing toluene. Nitrobenzene was prepared by the method used for mononitrotoluene. The resulting product was tested by conversion into aniline by the method outlined by Gattermann.[2] This section of the work was purely qualitative and no figures were obtained, but it may be stated that the preparations involved no difficulty and that the behavior of the benzene product was identical with that of the toluene.

Original Materials—The original materials were toluene fractions obtained from petroleum cracked by the Bureau of Mines vapor-phase process. The oils were distilled in commercial Badger stills. Analyses of the products yielded the following figures:

	Sample No. 1	Sample No. 2.
Distillation range	109°-115°	
Specific gravity (15°/15°)	0.832	0.823
Toluene content (on basis of sp. gr.) (*)	72.9%	66.4%

Preparation of Mononitrotoluene—The method employed for the preparation of mononitrotoluene was that of Schultz and Flachslander.[3]

> The nitration is conducted in a wide-mouthed, round-bottomed flask fitted with a thermometer (bulb immersed in the liquid) and with a short condenser, through which is passed a motor-driven stirrer. The nitrating acid is introduced through the condenser, being run in from a dropping funnel.
>
> For each 100 grams of toluene a mixture of 110 grams of nitric acid (sp. gr. 1.456) and 143 grams of sulfuric acid (sp. gr. 1.84) is required (the mixture made up in these proportions is hereafter designated as "mixed acid"). In the process of nitration the cold mixed acid is run in slowly from the dropping funnel. During the main course of the reaction the temperature is not allowed to rise above from 45° to 55°. At the end, when the concentration of excess acid is small, the mixture is heated to 100° in order to complete the nitration. It is claimed that by this method it is possible to obtain a yield which is 95 per cent of the theoretical.
>
> After completing the process of nitration the mixture is cooled and then washed with water to remove the remaining acid. The resulting oil is dried and distilled *in vacuo*. The use of vacuum or steam in the distillation does not permit the obtaining of actual boiling points but there is no necessity for this. A low boiling fraction comes over first, which includes the paraffins and any small residue of unnitrated toluene. The thermometer then starts to rise rapidly and at this point the receiver is changed. After the collection of a large fraction the temperature begins another sharp rise and the distillation is then stopped. The residue consists of resins and any di- or trinitrotoluene which may have been formed.

The experiments with mononitrotoluene were conducted to ascertain:

1—The effects of various methods of preliminary deolefinization;

2—The effect of variation in the quantity of nitrating acid upon the degree of purity;

3—The quantitative yields of the samples of mononitrotoluene obtained.

Details of these experiments are given in Table I. In Experiment 2, the sample of the toluene mixture was deolefinized by treatment with quantities of 10 and 5 per cent of its volume of ordinary concentrated sulphuric acid. The product was washed with water and alkali, dried and redistilled. A fraction was collected, boiling between 105° and 110°. This represented 75.2 per cent of the original and, on the approximately correct assumption that no toluene was lost in the preliminary treatment, it contained 97 per cent of actual toluene.

In Experiment 3 the sample of the toluene mixture was deolefinized as in Experiment 2, but the resulting mixture was nitrated immediately after drawing off the second lot of acid sludge.

Experiments 1, 2 and 3 established without any possible doubt the fact that by the simple process of nitration to the mono-stage, with subsequent distillation, it is possible to get rid of the impurities which are associated with aromatic hydrocarbons produced by the cracking of petroleum. The products obtained are pure within the limits of errors of analysis.

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[2] "Practical Methods of Organic Chemistry," second English from fourth German edition, 1907, p. 188.

*Rittman, Twomey and Egloff, Met. Chem. Eng., 13 (1915), 682.

[3] J. prakt. Chem., [2] 56 (1902), 156.

TABLE I—MONONITROTOLUENE FROM TOLUENE (100-GRAM SAMPLE—TOLUENE CONTENT AS GIVEN).
The Preliminary Treatments for Removal of Olefins Are Described in the Text.

					Yield of Purified (Distilled) Mononitrotoluene.					
					Grams Yield.		Per Cent Nitrogen ([a]).		Actual Per Cent.	
Type of Nitration—	Exp. No.	Mixed Acid. Grams.	Toluene Used. Grams.	Yield of crude mononitrotoluene. Grams.	Actual.	Theoretical.	Actual.	Theoretical.	Yield.	Purity.
Olefins present	1	253	72.9	95.0	79.0	108.5	10.16	10.21	72.7	99.5
Olefins removed, sample washed and redistilled	2	253	97.0	127.0	104.5	144.5	10.19	10.21	73.2	99.8
Olefins removed, no washing or redistillation	3a	253	88.5	127.0	86.4	131.8	10.19	10.21	66.6	99.8
	3b	253	79.2	126.0	76.8	118.0	10.17	10.21	65.3	99.6
Same as Experiment 3	4a	200	79.2	126.0	90.7	118.0	.....	10.21	77.3	....
	4b	200	76.2	120.0	90.0	115.3	10.04	10.21	79.3	98.5
Same as Experiment 3, but different sample	5a	180	68.8	126.0	84.4	102.5	.....	10.21	82.2	....
	5b	180	68.8	128.0	82.6	.....	.....	10.21	80.7	....

([a]) Nitrogen determinations were made under the direction of Mr. W. C. Cope of the Explosives Laboratory of the Bureau of Mines. Analyses were made by Mr. Cope's modification of the Kjeldahl method, which has been devised for nitro-substitution products. (Description about to be published.) The modification is characterized by a preliminary 12-hour cold digestion of the unknown substance with sulphuric acid, salicylic acid and zinc dust.

Correct indications as to the desirable method of preliminary treatment were obtained only by careful interpretation of results. It appears on superficial examination of the data obtained that the most desirable method on the basis of percentage yield is that which involves purification after the preliminary treatment with sulphuric acid. This is, however, undesirable from a commercial point of view. Mechanical difficulties arise on account of the formation of emulsions and, in addition, this treatment is unnecessary since the acid removed is immediately added again when the nitrating "mixed acid" is run in.

The next best yield was obtained when there was no preliminary treatment and this result furnished the key to a solution of this phase of the problem. The quantity of mixed acid used was calculated for 100 grams of actual toluene and as this amount of aromatic hydrocarbon was not present there was some conversion to dinitrotoluene, which substance is in the present course of procedure lost in the residue after distillation. When the preliminary deolefinization was omitted some of the nitric acid was taken up by the unsaturated bodies and the excess reduced, which resulted in an increased yield of mononitrotoluene. From a commercial point of view this is an undesirable mode of procedure since it involves allowing expensive nitric acid to do work which may be performed equally well by cheap sulphuric. It is obvious, however, that the magnitude of the yield is controlled by this factor of acid concentration and it appears that an excess is undesirable from the point of view of yield of the desired product as well as cost of wasted nitric acid. The conditions of preliminary treatment seem to have no effect upon the purity of the product, the general method of procedure being such as to fix this at high mark.

On the basis of general considerations of expense and convenience the process involving a simple refining with sulphuric acid and no intermediate washing before nitration seemed most desirable, even in face of the fact that it seemed to give lower yields than either of the two other methods. This low yield appeared to be explainable on the basis of excess of nitrating acid and Experiments 4*a* and *b* were therefore conducted to demonstrate whether or not this was the case. The indications furnished by these two experiments were clear-cut and satisfactory. To show that there was nothing accidental about them, and that they were not characteristic of the particular sample of toluene mixture used as original material, some supplementary preparations (experiments 5*a* and *b*) were made, using a second sample of toluene, which had a lower content of the aromatic hydrocarbon. The quantity of acid used was equivalent to that needed for 71 grams of toluene, so that a 3 per cent excess was present.

CONCLUSIONS REGARDING THE PREPARATION OF MONONITROTOLUENE.

1—Mononitrotoluene of a high degree of purity may be prepared from the paraffin-olefin-toluene mixtures obtained by the simple distillation of cracked petroleum. The purity of the nitro-product and, consequently, its utility for the preparation of water-washed trinitrotoluene, is fixed by the general method of treatment, which ensures a very sharp separation of mononitrotoluene from the impurities associated with it.

2—It is desirable to remove olefins by a preliminary extraction with sulphuric acid. Otherwise they consume expensive nitric acid and incidentally develop so much heat that the process of nitration is difficult to regulate. No washing is necessary between the processes of deolefinization and nitration since such a treatment removes acid which must be added again as soon as nitration is begun.

3—The quantity of nitrating acid mixture should be based approximately on the actual toluene in the mixture to be treated and not on the total quantity of the latter. An excess of acid causes the formation of dinitrotoluene, which under present conditions is an undesirable occurrence.

PREPARATION OF TRINITROTOLUENE.

Experiments on the preparation of trinitrotoluene were not conducted for the purpose of modifying or improving any of the numerous methods which have already been proposed. The work done was for the simple purpose of obtaining absolute verification of the results obtained by the analysis of the samples of mononitrotoluene prepared by the method indicated above. The fact to be established was that the fraction of a per cent of impurities included in the mononitro product did not in any unexpected way interfere with its transformation into water-washed trinitrotoluene of a satisfactory degree of purity.

Preliminary experiments were performed according to various sets of directions found in the literature, but the products obtained invariably melted below the required mark of 75° C. A satisfactory product could always be obtained by a simple crystallization from alcohol but this fact was of little significance.

It finally appeared necessary to concentrate on the details of some specific method and for this purpose the poly-stage process employed by one of the large explosives companies in this country was selected as most promising. Translated into terms of quantities usable in the laboratory the method of procedure is as follows:

First Stage—Transformation of mononitrotoluene into dinitrotoluene:

Amount of mononitrotoluene	50 g.
Acid concentration	107.6 g. of a mixture of 1 part by weight of HNO_3 (sp. gr. 1.5) and 2 parts H_2SO_4 (sp. gr. 1.84).
Temperature during addition of acid	88.0° C.
Time of heating	½ hour at 88.0° C.

The mixture is then cooled and the spent acid drawn off.

Second Stage—Transformation of unpurified dinitrotoluene into trinitrotoluene:

Acid concentration	67 g. of "oleum" (fuming sulfuric acid containing an excess of 20 per cent of SO_3 over ordinary conc. H_2SO_4). 42 g. of nitric acid (sp. gr. 1.5).
Temperature during addition of acid	Below 88.0° C.
Heating	1 hour at 88.0°. 1½ hours at 100°.

The mixture is then cooled and the acid drawn off. The remaining product is washed several times with hot water, being stirred with the latter while in a molten condition. It is finally dried.

The first experiments were performed using the quantities of acid specified in these directions but with modifications in the time and degree of heating (Nos. 1 to 4, Table II):

TABLE II.—TRINITROTOLUENE FROM MONONITROTOLUENE.

First Stage Mono- to Dinitrotoluene Acid Specified.			Second Stage: Di-to Trinitrotoluene Acid in Excess of Amount Specified							Yield	
				Hours heated at Temperatures (° C.)							
Exp. No.	Heated Hrs.	Temp. ° C.	% Excess Acid.	95	100	110	115	120	130	In grams.	Melting point (a). ° C.
1	1	88	0	1	1½	0	0	0	0	64	57 -72
2	1	88	0	1	1	0	½	0	0	61	58 -69
3	1	88	0	1	1½	½	0	½	½	61	55 -72
4	½	115	0	1	0	0	0	1½	0	60	69 -77
5	½	115	25	1	1½	1	0	½	0	60	73.5-77.5
6	½	115	25	1	0	0	0	1½	0	58	75 -79
7	1	115	50	1	1½	0	0	0	0	60	74 -80
8	1	115	50	1	1½	0	0	0	0	56	75.5-79.5
9	1	115	50	1	4	0	0	0	0	60	75.5-79
10	½	115	50	1	0	0	0	1½	0	60	78 -79.5

(a) Melting points were determined under the direction of Mr. Cope in the Explosives Laboratory of the Bureau of Mines. Thermometers were carefully standardized. The apparatus was that described by Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. I (1908), p. 218.

This series of experiments was instructive, since it appeared that no improvement could be secured through increasing time of heating and temperature in the second stage of the process. A marked improvement, however, appeared by the modification of treatment in the first stage. Heating for one-half hour at 115° instead of an hour at 88° resulted in an increase of about 10° in the melting point of the product.

The next series of experiments involved a 25 per cent increase in the amount of acid used for the second stage of the nitration (Nos. 5 and 6, Table II). An improvement was shown here, the product obtained in one case being just above the satisfactory degree of purity.

From a commercial point of view there seems to be no inherent objection to the employment of a considerable excess of acid at the second stage of the reaction, since the spent acid may be utilized in an earlier stage in the next cycle. Hence, instead of proceeding with experiments involving a 25 per cent excess of acid, the quantity was increased to a 50 per cent excess and a third series of preparations made (Nos. 7-10, Table II). Three of these four experiments yielded satisfactory products and there seemed to be no doubt but that with the higher concentration of acid there was little difficulty in producing a trinitrotoluene of a satisfactory degree of purity. The yields were all in the neighborhood of 60 grams, which is about 70 per cent of the theoretically possible amount. This is, of course, low, for commercial work, but conditions here were less favorable than they would be on a large scale and, at best, the work has only remotely approached completion in the matter of determining optimum condition for the process of nitration. Here as well as in the earlier part of the work, attention was given only to the establishment of general principles and no attempt was made to learn details.

CONCLUSIONS REGARDING THE PREPARATION OF TRINITROTOLUENE.

1—Trinitrotoluene, of a satisfactory degree of purity, may be prepared from the mononitrotoluene obtained by the nitration of the toluene-paraffin-olefin mixtures, produced by the fractionation of "cracked" petroleum.

2—From the laboratory point of view, at least, the poly-stage process seems best. The transformation from mono- to di-product should involve a fair degree of heating and a moderate concentration of acid. The final stage of the nitration should be conducted with a considerable excess of strong acid, which acid need not be wasted since when drawn off it may be used in an earlier stage of the next cycle of nitration.

GENERAL SUMMARY.

I—The aromatic hydrocarbons produced by the "cracking" of petroleum may be utilized for the preparation of nitro-products without being brought to a high degree of purity. The foreign substances not easily removable are paraffins and these are not affected by reagents of sufficient vigor to transform the aromatics quantitatively into mono-nitro products. These compounds may be separated in a high degree of purity by a simple process of distillation.

II—The mononitrotoluene prepared by the method indicated may be readily converted into trinitrotoluene which, when washed with hot water, satisfies the ordinary commercial specification of a melting point of 75° C.

According to an announcement of the U. S. Coast and Geodetic Survey invar metal, formerly not made in the United States commercially, is now obtainable from an American manufacturer. It is an alloy of nickel and iron and valuable because of its very low coefficient of expansion, about 1/25 that of steel. Tapes of this metal for use in base measurement have been obtained from England as required.

TERMS OF CONTRACTS FOR WAR MUNITIONS.*

So much unnecessary secrecy and mystery have been attached to the manufacture of war munitions that many erroneous impressions are current in relation to the contracts under which they are produced. In reality, however, considering the great issues and amounts of money involved, these contracts are extraordinarily simple in their terms, and any one of them can be understood by the average manufacturer without difficulty.

Taking projectiles as the subject of most general interest, it may be said that contracts for either shrapnel or high explosive shells specify: 1, the government interested or the agent acting in its behalf; 2, the seller; 3, the total quantity or quantities to be delivered and the prices agreed upon for each; 4, the dates at which deliveries are to commence and be maintained, usually expressed in certain quantities monthly after a definitely fixed period of preparation.

The manufacturer, when ready to begin deliveries, is required to notify the agent of the purchasing government in writing. He will then be given written instructions covering the shipment of the shells; or, in the event that such instructions are not received within ten days after the notification of the manufacturer of his readiness to make deliveries, the shells manufactured may be put in storage for the account of the government concerned, all storage charges, if any, to be borne by the latter. Delivery f. o. b. at the works of the seller is usually specified, but freight allowance to New York City docks may be demanded.

SAFEGUARDS FOR PURCHASERS AND MAKERS.

Within two days of signing the contract, the purchaser will pay 25 per cent of the total amount into the bank with which the manufacturer has a deposit account or other bank mutually agreed upon between the parties. This represents the *final* payment to be made under the contract and all but 5 per cent of it is inviolate for that purpose, this 5 per cent representing the maximum of penalties which it is possible for the purchaser to assess, as stated below.

The fund for the remaining 75 per cent, which will be covered by monthly payments in full for all quantities delivered, is established as a guaranteed, irrevocable dollar credit with a metropolitan bank acceptable to the seller. Payments from this credit are made upon presentation of invoices in triplicate, accompanied by bills of lading and proper certificates of inspection; or, in case shipping directions are not promptly received, there may be substituted receipts signed by the manufacturer to the effect that deliveries are being held in storage subject to the order of the purchasing government.

The bank representing the seller in turn binds itself, by suitable instruments, to the banking house with which the purchaser's credit is established, that in case of non-delivery of the shells in payment for which the cash was advanced the whole or a proportionate amount of it to cover the delinquent deliveries will be refunded. This makes it necessary to hold the 25 per cent deposit until the last.

Where, however, there is no question in the local banker's mind about the good faith of the seller and his ability to fulfill his part of the contract, it is customary to loan him up to 20 per cent of the amount placed on deposit. This accordingly serves as a fund with which to provide any new equipment or plant buildings needed and get ready to turn out the shells. As deliveries begin to pass the last quarter, a proper proportion of four-fifths of the deposit can also be released.

As a part of the contract to make deliveries within the time limits imposed by the contract, the manufacturer agrees to pay as liquidated damages for each day in excess of 30 days' delay, one-fourth of 1 per cent of the value of all shells which he has failed to deliver in the 30 days after such delivery was due. But the reservation is expressly made and agreed to by the purchaser that "should such failure to deliver the shells guaranteed be due to a breakdown in the seller's plant, or to strikes, to the destruction of the seller's plant from fire or explosion, to the act of God or to some result from any other unavoidable cause, the penalty provided for shall not apply." In that event the contract is merely to remain suspended during the time of such disability on the part of the seller to make deliveries. Furthermore, it is provided that the total penalties under the contract shall not exceed 5 per cent of the value of all the shells which it covers "and that no other penalty may be exacted": except, of course, as rejections may be considered in that class.

INSPECTION.

All inspections are to be made by representatives of the purchasing government at the plant where the shells or shell parts are manufactured. In case of disputes over the findings of any of the inspectors, the decision of an umpire or referee appointed in a manner mutually agreed upon by the contract parties is to be taken, the fees of the referee to be paid by the loser of the decision. All penalties are subject to suspension until the referee makes his decision. This referee, which is usually one of the well-known bureaus of inspection and tests, is customarily named directly in the contract.

The above constitutes all of the general terms of a shell contract; but they are considerably enlarged upon by the specifications for the shells themselves, which are attached to and form part of the agreement. After a manufacturer is once well started on production, this is where the rub comes, if any.

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*From The Iron Age.

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NOTES AND COMMENTS.

Solving the Potash Problem.

Several new methods of increasing the supply of American potash have recently been brought to the attention of the Bureau of Foreign and Domestic Commerce. One of the most promising of these efforts to find a substitute for German fertilizers is a patent taken out a few weeks ago by a Canadian for a method of using the potash in ordinary feldspar.

The process is a simple one, consisting of heating the feldspar with limestone and iron oxide at a temperature of about 2,200° Fahr., which produces a partly fused mass that is easily decomposed by a weak acid. From this product the potash salts can readily be extracted for further purification. The inventor has been in consultation with Dr. Norton, the expert who has been looking after the potash and dyestuff situations for the Bureau of Foreign and Domestic Commerce, and it seems very possible that a greatly simplified method of transforming feldspar into fertilizer will soon be available.

A practical try-out for another method of obtaining potash fertilizer will soon take place at a New Orleans distillery where molasses is used in large quantities. It is a fact that 106 tons of potash are wasted daily by the 25 or more distilleries in this country that subject molasses to processes of fermentation. The New Orleans company is planning to install the process of saving the potash in distillery waste recently brought to the attention of the public by the Bureau of Foreign and Domestic Commerce. It should be possible to make fertilizer from this otherwise worthless material at a price that will meet competition even after the war is over.

Bureau of Standards Studies Specimens of Bronze.

The quality of metal castings is usually determined by measuring the properties of a test specimen cast from the same metal. The United States Bureau of Standards has completed an investigation of the various foundry operations that influence the properties of the test specimen, for one of the most generally used commercial alloys, known as Government bronze, having the composition 88 copper, 10 tin, and 2 zinc. The bureau studied the effects of temperature on casting, methods of gating, casting, molding, kind of sand, heat treatment, and the effect of similar factors upon the resulting mechanical properties. A microscopic examination of the fractured test specimens showed that the most common source of weakness was the occurrence of oxides within the metal. Such oxides appear frequently as thin films throughout otherwise sound metal, producing a condition of brittleness and low ductility. This investigation will be published as a Technologic Paper of the Bureau of Standards, and may be obtained by application to the bureau, at Washington, D. C.

Superior U. S. Clay Makes Industry Independent.

American glass manufacturers who have felt the necessity of depending upon foreign clays will be able hereafter to assert their independence of foreign material, as a result of experiments that have been conducted by the United States Bureau of Standards. The Pittsburgh laboratory of that bureau, which is located near one of the chief centers for the industry in the United States, working in co-operation with the clay-pot industries, has learned that glass refractories (pots in which the glass is melted) can be prepared from American clays, with resulting better quality than that of the article manufactured with the addition of German plastic clays. The mixture prepared from American clays proved superior in the glass-corrosion tests, both to the mixtures prepared with German clays alone, and to those prepared from American and German clays combined. The director of the Bureau of Standards states that the value of the results of this single investigation to American industry far surpasses the entire amount the Government has expended in the clay-products work since the time of reorganization The opinion of those in charge of the experiments is that from now on no foreign clays will be needed in this branch of manufacture. The work inaugurated by these experiments is now ready to be tried out on a large scale.

RUBBER SHIPMENTS FROM AMAZON VALLEY.

Exports of Amazon Valley crude rubber to the United States during September, according to Consul George H. Pickerell, Para, Brazil, were 78 per cent greater than in the corresponding month of last year; exports to Europe were about 8 per cent less. Each of the four grades of rubber sent to the United States showed gains over September, 1914, but only in "fine" was there any increase in the cargoes to Europe. By ports the month's shipments were:

Exported from—	Fine. Pounds.	Medium. Pounds.	Coarse. Pounds.	Caucho. Pounds.	Total. Pounds.
Para to—					
United States	1,018,668	301,015	769,856	205,592	2,295,131
Europe	538,300	6,958	40,300	20,080	605,638
Manaos to—					
United States	1,411,377	128,783	236,503	351,822	2,128,485
Europe	156,703	55,828	24,138	20,701	557,370
Itacoatiara to—					
United States	....	....	....	....	....
Europe	18,938	1,080	8,047	5,159	33,224
Iquitos, Peru, to—					
United States	87,949	3,695	51,861	117,002	240,507
Europe	....	....	....	....	....
Total, September, 1915, to—					
United States	2,517,994	433,193	1,038,220	674,416	4,664,123
Europe	1,013,941	63,866	72,485	45,940	1,196,232
Total, September, 1911, to—					
United States	1,243,868	216,038	702,657	453,916	2,616,479
Europe	936,235	95,619	103,666	161,407	1,296,927
Grand total, September, 1915	3,531,935	497,359	1,110,705	720,356	5,860,355
Grand total, September, 1911	2,180,103	311,657	806,323	615,323	3,913,406

Swiss Dye Makers' Profits.

The report of the Society of Chemical Industry, Basel, the largest of the Swiss color firms, states the Manchester Guardian, shows a net profit (after providing $535,000, as against $175,000 last year, for depreciation, and placing $195,000 towards a new pensions fund) of $496,000, as against $350,000. It is proposed to pay 16 per cent, as against 6 per cent and previous dividends of 10 per cent. Stocks are valued at $462,000 only, as against $1,324,000 last year, due to the demand for dyestuffs being so brisk that virtually no stocks are now held. The Clayton Aniline Co., Manchester, which is controlled by the Basel concern, is stated to have been very well occupied throughout the year, and the financial results have quite come up to expectations. A holding has been acquired in the Swiss Soda Works, Zurzach, a company formed for the manufacture of soda ash and caustic soda. This is the first undertaking of its kind in Switzerland, previous supplies of these chemicals having been obtained from Germany.

Saving the Waste In Coke Making.

By-products from retort coke ovens in the United States in 1914 included 61 billion cubic feet of gas worth 6 million dollars, 110 million gallons of tar worth 24-5 million dollars, 73-5 million dollars' worth of ammonia, and 1 million dollars' worth of benzol, etc. However, 57 per cent of the coke production of the country—35 million tons in 1914—still comes from the old-style beehive oven. About two-thirds of the gas saved is used industrially, but over 50 million cubic feet is sold daily for domestic purposes. Almost the entire supply of gas in some cities is from retort coke ovens. Among these cities are Boston, Mass.; Camden, N. J.; Indianapolis, Ind.; Hamilton, Ohio; Baltimore, Md.; Duluth, Minn.; South Chicago, Ill.; and Milwaukee, Wis.

Content of Gasoline Vapor In Air Determined.

Two methods for determining the content of gasoline vapor in air have been the subject of experiments and a report by the United States Bureau of Mines. In one the mixture is introduced into an exhausted glass vessel, is cooled at the temperature of liquid air, the air is removed, and finally the partial pressure of the gasoline vapor is measured by means of a manometer attached to the liquefaction bulb. The second method consists in burning the gasoline vapor in oxygen and from the contraction and carbon dioxide produced calculating the percentage of gasoline vapor. Copies of Technical Paper 115, "The inflammability of mixtures of gasoline vapor and air," which has just been issued, may be obtained by applying to the Bureau of Mines, Washington, D. C.

WANTED POSITION—By experienced industrial chemist. Fertilizer, steel, iron, coal, etc., preferred. Employed but desire a change. References furnished. Address "Analysis," care The Chemical Engineer, Chicago, Ill.

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